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THE UNIVERSITY OF ALBERTA

A STUDY OF THE OXYGEN-18 CONTENT IN PRECIPITATION AT

EDMONTON, ALBERTA

by



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A THESIS

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THE UNIVERSITY OF ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "A study of the Oxygen-18 Content in Precipitation at Edmonton, Alberta" submitted by John Charles Linton in partial fulfilment of the requirements for the degree of Master of Science.

Date.....*MAY 5, 1972*.....

ABSTRACT

In recent years many studies in fields related to Meteorology have been done using Oxygen-18 and Deuterium Isotopes. These fields include Glaciology, Paleoclimatology, Cloud Physics, and Hydrology. In this thesis some of the local processes that influence the Oxygen-18 content measured in precipitation are examined, with the ultimate goal of using Oxygen-18 as a tracer of the history of the water vapour that is condensed for local precipitation.

Dansgaard considered the mean annual δ values in precipitation of coastal stations, and found that they were linearly related to the mean annual temperature by the equation

$$\bar{\delta} = 0.695 \bar{T} - 13.6 \text{ ppt}$$

By applying linear regression to the mean monthly δ values and mean monthly temperatures for only the summer months (May through September) at Edmonton, Alberta it is found that they are related by

$$\bar{\delta} = 0.37 \bar{T} - 20.0 \text{ ppt}$$

After exploring theoretically some of the physical processes that cause isotopic fractionation in precipitation, models are developed to show how these processes modify the δ values measured in precipitation. This modelling includes both saturated-pseudoadiabatic cooling and evaporation and exchange processes acting on the raindrops between the cloud base and the ground. With these models it is shown that the isotopic fractionation during cooling is

dependent upon the liquid water content of the cloud and the initial temperature of the saturated air. This fractionation is shown to be less than that obtained by using the models of Miyake, Matsubaya, and Nishihara who considered dry adiabatic cooling. It is also shown that evaporation and exchange can cause changes of the order of two parts per thousand under summer conditions.

Grouping the data by individual periods of precipitation showed the variations in δ values of precipitation that occur with time. It is found that different types of storms exhibit different variations of δ values with time. For an airmass thunderstorm the δ values of the precipitation are found to decrease markedly during the storm. Attempts to explain this time change in δ values were made using the thunderstorm model of Byers and Braham along with the models that were formulated in this study. The changes in time of the δ values of precipitation during general periods of rain are found to be small and are ascribed to evaporation and exchange processes.

In this study it was found that the data available were insufficient to permit the removal of the local changes from the measured δ values. It is recommended that further sampling be undertaken so that future work may establish if tracer techniques are feasible using Oxygen-18.

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TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	viii
LIST OF TABLES	x
Chapter	Page
I. INTRODUCTION	1
1.1 The Isotopes of Oxygen	1
1.2 Areas of Study Related to Meteorology	1
1.3 Variations in Oxygen-18 Abundance	2
II. THEORY	6
2.1 Introduction	6
2.2 Fractionation	6
2.3 Equilibrium Processes	7
2.4 Kinetic Processes	8
2.5 Equilibrium Exchange Effects	9
III. MODELLING	11
3.1 Introduction	11
3.2 Adiabatic Condensation	11
3.2.1 Model 1	13
3.2.2 Model 2	14
3.2.3 Model 3	14
3.2.4 Model 4	16
3.2.5 Results	17

Chapter	Page
3.3 Evaporation	21
3.3.1 Results	29
3.4 Exchange Effects	31
3.4.1 Results	31
IV. THE DATA	34
4.1 Collection Methods	34
4.2 Analysis Methods	35
V. DISCUSSION AND RESULTS	39
5.1 Introduction	39
5.2 General Results	39
5.3 The Change in Del Values with Time	42
5.3.1 Instability Precipitation	43
5.3.2 General Precipitation	46
5.4 An Alternate Approach	50
VI. CONCLUSIONS AND RECOMMENDATIONS	61
6.1 Conclusions	61
6.2 Recommendations for Further Studies	62
BIBLIOGRAPHY	64
APPENDIX A	66
APPENDIX B	79

LIST OF TABLES

Table	Page
1. A summary of the samples collected during the summer months.....	41
2. A summary of the changes of del values that occurred below cloud base, including the effect of a change of initial drop concentrations.....	57
A-1 A listing of all samples collected.....	72
A-2 The site code.....	78
A-3 The weather (WX) code.....	78

LIST OF FIGURES

Figure	Page
1. Mean monthly del values versus mean monthly temperature at Edmonton, Alberta for the summer months.....	3
2. Del values as a function of temperature for pseudoadiabatic cooling (models 1 and 2).....	18
3. Del values as a function of temperature for pseudoadiabatic cooling (model 3).....	19
4. Del values as a function of temperature for pseudoadiabatic cooling (model 4).....	20
5. The effect of changing the initial temperature for model 3.....	22
6. A comparison of the wet models to the dry models during cooling.	
(a) Model 1.....	23
(b) Model 2.....	24
(c) Model 3.....	25
(d) Model 3.....	26
(e) Model 4.....	27
7. The variation of del values of raindrops during descent for equilibrium evaporation.....	30
8. The variation of del values of raindrops during descent for kinetic evaporation.....	32
9. The variation of del values of raindrops during descent for equilibrium exchange.....	33
10. A sample of the computer output for the analysis of a sample....	37
11. Mean monthly del values versus mean temperature for the collected samples.....	40
12. Time variations in the del values of precipitation associated with an airmass thunderstorm on July 23, 1971.....	44
13. Time variations in the del values of precipitation associated with a non-airmass thunderstorm on August 13, 1970.....	45
14. Time variations in the del values of precipitation associated with warm frontal rain on September 1, 1970.....	47
15. Time variations in the del values of precipitation associated with cold-low precipitation on June 5, 1971.....	48
16. Time variations in the del values of precipitation associated with cold-low precipitation on June 14-18, 1971.....	49

Figure	Page
17. The effect of liquid water content on the del values of cloud droplets during cooling.....	52
18. The effect of cloud base temperature on the del values of cloud droplets during cooling.....	53
19. The combined effect of liquid water content and cloud base temperature on the del values of cloud droplets during cooling	54
20. Final del values of raindrops due to equilibrium exchange.....	55
21. Final del values of raindrops due to equilibrium evaporation..	58
22. Final del values of raindrops due to kinetic evaporation.....	59
23. Percentage of the initial change in del value of raindrops exhibited by the final raindrops.....	60
A-1 Time variations in the del values of precipitation associated with an airmass thunderstorm on July 20, 1970.....	67
A-2 Time variations in the del values of precipitation associated with an airmass thunderstorm on July 20, 1970.....	68
A-3 Time variations in the del values of precipitation associated with a non-airmass thunderstorm on July 9, 1970.....	69
A-4 Time variations in the del values of precipitation associated with a period of general rain on June 14-16, 1971.....	70
A-5 Time variations in the del values of precipitation associated with a period of general rain on July 29, 1970.....	71

CHAPTER 1

INTRODUCTION

1.1 The Isotopes of Oxygen

In nature there exist three stable isotopes of the oxygen atom. They have atomic weights of 16, 17, and 18 atomic mass units and may be designated as ^{16}O , ^{17}O , and ^{18}O , respectively. The most abundant isotope is ^{16}O with ^{17}O , having an odd atomic weight, being the least abundant in natural sources. In natural waters it has been found that the abundance of ^{18}O is approximately two parts per thousand (hereafter designated as ppt) (Dansgaard, 1953, 1964).

1.2 Areas of Study Related to Meteorology

Oxygen -18 concentrations have been used in various fields related to meteorology. One such field is Glaciology. Workers such as Confiantini et al. (1963) have studied the variations in ^{18}O concentration that occur in the different layers of a glacier. These variations have been correlated with the stratigraphy and have shown annual variations. Epstein and Sharp (1959) used the variations in ^{18}O concentrations with position in the glacier along with a model of glacier movement to show how ^{18}O concentrations could be used in glacier flow studies.

More recent studies in glaciology by Dansgaard et al. (1969) and Epstein, Sharp, and Gow (1970) have been related to past climate. These workers have taken deep core samples through the ice caps of Greenland and Antarctica, respectively. Dansgaard et al. (1969) found variations in ^{18}O concentration dating back 100,000 years. In these results the variations due to the Pleistocene Ice Age and

climatic changes since that time were shown. Epstein et al. (1970) found similar results in Antarctica.

Further work has been done in studying the ^{18}O concentration variations in hailstones. Workers such as Macklin, Majoube, and Merlivat (1972), Macklin, Merlivat, and Stevenson (1970), and Majzoub, Nief, and Roth (1968) used a model to explain the change in ^{18}O concentration with temperature in a hail-producing cloud. With this model and the observed ^{18}O variations in the hailstones they were able to infer the trajectories of the hailstones within the cloud.

Dansgaard (1964) studied the mean annual ^{18}O concentrations in precipitation at stations, for which data were available, located around the North Atlantic Ocean. By comparing these mean annual values with the mean annual surface temperature for the station, he developed the empirical relation

$$\bar{\delta} = 0.695 \bar{T} - 13.6 \text{ ppt} \quad (1.1)$$

where $\bar{\delta}$ is the annual mean of a measure of ^{18}O concentration (to be defined in Chapter II), and \bar{T} is the mean annual temperature in degrees Celsius.

1.3 Variation in Oxygen -18 Abundance

Oxygen isotope and temperature data for Edmonton, Alberta were compared with the linear relation given by Eq. (1.1). Because annual values are available for only three years (1963 - 1965), it was assumed that mean monthly values would yield the same relation. Figure 1 shows the mean monthly δ values (δ) plotted with respect to the mean monthly temperature data collected between May and September in

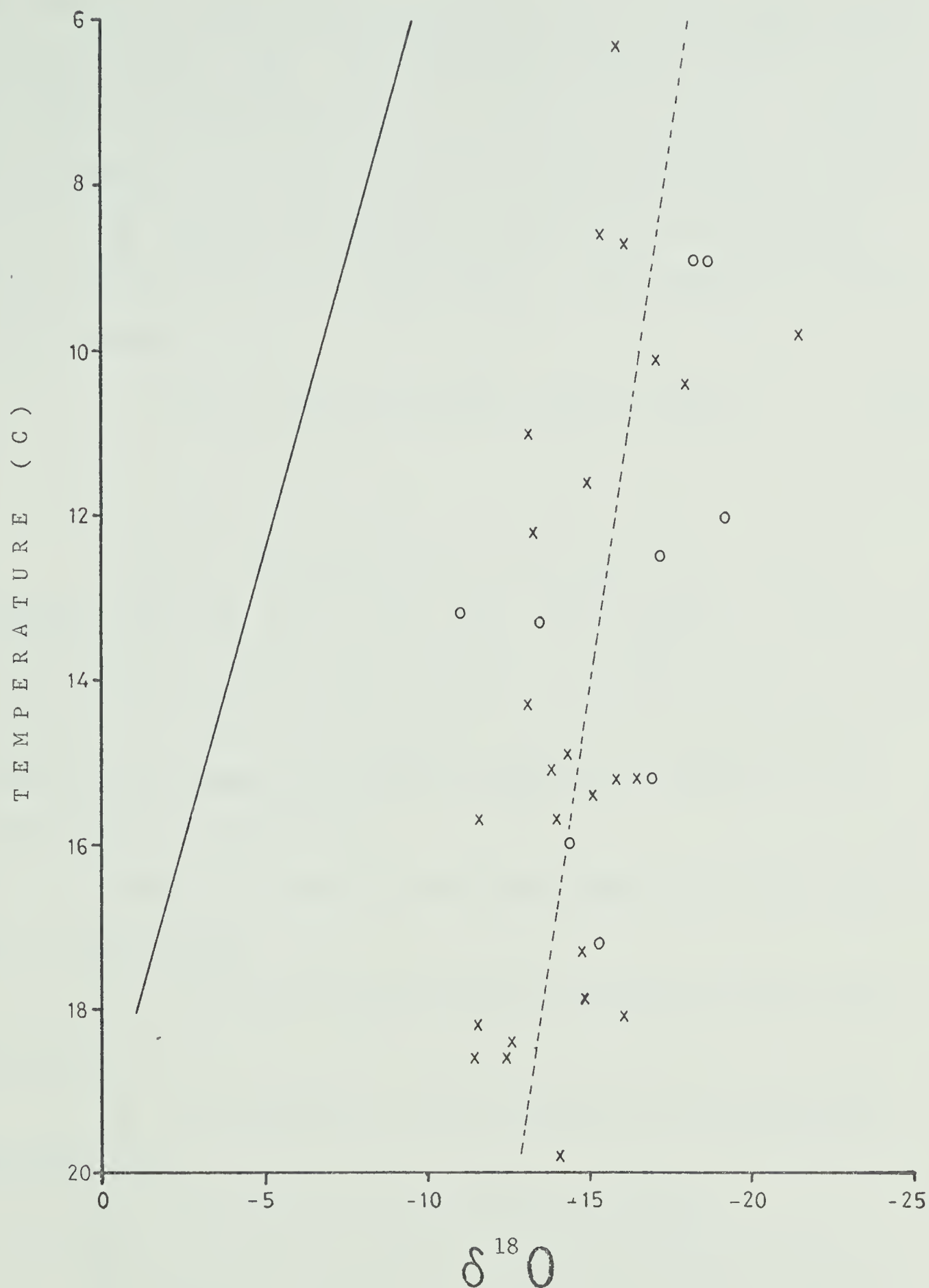


Figure 1. Mean monthly $\delta^{18}O$ values versus mean monthly temperature at Edmonton, Alberta for the summer months. (X) 1961-1965, (O) 1970-1971. Solid line is Eq. (1.1), dashed line is Eq. (1.2).

the years 1961 to 1965 (from International Atomic Energy Agency, 1969, 1970) and in 1970 - 1971. It is immediately apparent that all of the δ values are below the straight line value of Eq. (1.1). It must be noted, however, that at least part of the observed difference could well be due to the change from considering annual values to considering monthly values for only the summer months. Linear regression applied to the data gave

$$\bar{\delta} = (0.37 \pm 0.10) \bar{T} - 20 \pm 2.0 \text{ ppt} \quad (1.2)$$

When this study was begun it was thought that possibly relations such as Eq. (1.1) or Eq. (1.2) could be applied to use ^{18}O concentrations in precipitation as a tracer to study the source of water vapour for local precipitation. It was felt necessary to consider other possible mechanisms to explain the variations in ^{18}O concentration in precipitation.

Several such mechanisms have been identified in the literature. These include:

- 1) the isotopic composition of the original source of the water vapour,
- ii) the temperature at which evaporation and condensation processes occur,
- iii) the method of evaporation from the source,
- iv) the past condensation history of the vapour between evaporation at the source and condensation into precipitation,
- v) the effects caused by the mode of transport (ie, eddy diffusion or advection) of the vapour from the source region, and

vi) exchange and evaporation processes acting on the raindrop between formation and analysis.

Most of these influences will be examined in Chapters III to V after considering some of the theory of ^{18}O concentrations in Chapter II.

CHAPTER II

THEORY

2.1 Introduction

As stated in Chapter I the abundance of ^{18}O is approximately two ppt in natural waters. Absolute concentrations are difficult to obtain. However, because it is only the variations in ^{18}O content that are of interest, a relative change in content is measured. Thus the relative deviation, or δ value, (denoted by δ) of the ^{18}O content of a sample from a reference standard is measured. Thus

$$\delta = \left[\frac{C_{\text{sample}}}{C_{\text{standard}}} - 1 \right] \times 10^3 \text{ ppt} \quad (2.1)$$

where C is the ratio of mole fractions of H_2^{18}O to H_2^{16}O in the water (hereafter referred to as the oxygen ratio). The reference standard used is SMOW (Standard Mean Ocean Water) (Craig, 1961).

If a sample has a deviation of δ' relative to a secondary standard that has a deviation of δ_s from SMOW, Dansgaard (1964) gave that the sample's deviation relative to SMOW is

$$\delta = \delta' + \delta_s + (\delta'\delta_s/10^3) \text{ ppt} \quad (2.2)$$

2.2 Fractionation

Isotopic fractionation of water occurs whenever water undergoes a change of phase from vapour to liquid or solid and for the reverse change of phase. This is due to H_2^{16}O having a higher vapour pressure than has H_2^{18}O . A fractionation factor α is defined as

$$\alpha = C_L / C_V \quad (2.3)$$

where C_L and C_V are the oxygen ratios in the liquid and vapour phases, respectively. If the vapour pressures of $H_2^{16}O$ and $H_2^{18}O$ are denoted as e_{16} and e_{18} , respectively, then the fractionation factor can be approximated by

$$\alpha = e_{16}/e_{18} \quad (2.4)$$

for equilibrium conditions. Because the temperature dependencies of e_{16} and e_{18} are not the same, the fractionation factor is also temperature dependent, having values of approximately 1.007 at 40 C and 1.014 at -20 C (Dansgaard, 1964).

2.3 Equilibrium Processes

To demonstrate how the oxygen ratio can vary in space and time several processes will now be considered.

A closed system, such that the total vapour and liquid phases are in equilibrium, will now be considered. If a small amount of vapour is condensed in this closed system, the newly-formed condensate has an oxygen ratio that follows Eq. (2.3) and thus the vapour becomes depleted in ^{18}O . With further condensation both the vapour and the newly-formed condensate become more depleted in ^{18}O .

Under atmospheric conditions the total condensate does not stay with the vapour, but falls relative to the vapour. For a system that is closed except that the condensate is immediately removed, so that no exchange occurs between the liquid and vapour phases, Rayleigh condensation occurs (Dansgaard, 1964). Then for the condensation process

$$\frac{dC_V}{C_V} = (\alpha - 1) \frac{dN_V}{N_V} \quad (2.5)$$

where N_V is the mass of vapour in the system. As shown by Dansgaard (1964) this leads to greater fractionation of the oxygen isotopes, with both the remaining vapour and the newly-formed condensate becoming more depleted in ^{18}O than would be the case according to Eq. (2.3).

For evaporation of a fixed finite sample of liquid, the oxygen ratio of the liquid changes according to an equilibrium batch distillation such that

$$C_L = (C_L)_0 F^\epsilon \quad (2.6)$$

where $(C_L)_0$ is the initial oxygen ratio in the liquid, F is the fraction of the liquid remaining, and

$$\epsilon = \frac{1}{\alpha} - 1 \quad (2.7)$$

(Craig, Gordon, and Horibe, 1963, Eq. 1). As $F \leq 1$ and $\epsilon < 0$, Eq. (2.6) leads to continued enrichment of ^{18}O in the remaining liquid as the sample evaporates.

2.4 Kinetic Processes

In atmospheric conditions condensation can be regarded as a slow process and thus equilibrium conditions as discussed above will hold. Evaporation, however, is in some cases a fast process and kinetic effects must be considered. These influences are due to the difference in diffusivities for H_2^{18}O and H_2^{16}O in both the liquid and the vapour phases. These differences influence the fractionation during evaporation.

Ehhalt and Knott (1965) derived the equation

$$\alpha_K = \left(\frac{D}{D'}\right)^{1/2} \left(\frac{1-h'}{1-h'\alpha_D C_V/C_D}\right) \quad (2.8)$$

for the kinetic fractionation factor α_K , where D' and D are the diffusivities of $H_2^{18}O$ and $H_2^{16}O$, respectively in air, h' is the relative humidity of the air measured relative to the drop temperature, α_D is the equilibrium fractionation factor at the drop temperature, and C_V and C_D are the oxygen ratios in the air and drop, respectively. The effective fractionation factor, α_E is then

$$\alpha_E = \alpha_D \cdot \alpha_K \quad (2.9)$$

Because α_K is usually greater than unity, the use of the effective fractionation factor in Eq. (2.6) leads to greater distillation than equilibrium conditions.

2.5 Equilibrium Exchange Effects

A droplet of water in air containing water vapour is subject to an equilibrium exchange of water molecules between the droplet and the vapour even when no net mass transfer occurs. Thus the droplet can experience a change in the oxygen ratio if the oxygen ratio of the vapour is not related to the droplet's oxygen ratio by Eq. (2.3) when the fractionation factor is evaluated at the droplet temperature.

For this exchange Friedman, Machta, and Soller (1962) and Miyake, Matsubaya, and Nishihara (1968) developed the equation

$$m - m_F = (m_i - m_F) \exp(-kt) \quad (2.10)$$

where m is the amount of $H_2^{18}O$ in a droplet, subscripts i and f denoting initial and final stages, respectively, t is the duration time of the exchange, and k is the rate constant for the reaction given by

$$k = \frac{3D\theta PM}{r^2 \alpha \rho R^* T} \quad (2.11)$$

where P is the saturated vapour pressure of normal water at temperature T (in this and further equations in degrees Kelvin), R^* is the universal gas constant, M is the molecular weight of $H_2^{18}O$, r is the radius of the droplet, ρ is the density of the droplet, and θ is the ventilation factor of a falling droplet developed by Kinzer and Gunn (1951),

$$\theta = 1 + \frac{F Re^{1/2}}{(4\pi D/\nu)^{1/2}} \quad (2.12)$$

where F is an empirical factor of Kinzer and Gunn, Re is the Reynolds Number, and ν is the kinematic viscosity of the air.

Because cloud droplets are small, giving a relatively large rate constant, the exchange process will keep the cloud droplets essentially in equilibrium with the surrounding vapour. For large raindrops the rate constant becomes relatively small, so that longer adjustment times are required to reach equilibrium with the surrounding vapour. Thus raindrops are seldom in equilibrium with the vapour, but they are modified by this process.

CHAPTER III

MODELLING

3.1 Introduction

In an attempt to explain the local effects on the oxygen ratio that appeared in the data collected, a computer model of the theoretical variations of the oxygen ratio was developed. This model included both adiabatic condensation of water vapour and modification of the oxygen ratio in falling raindrops due to exchange and evaporation.

3.2 Adiabatic Condensation

Miyake, Matsubaya, and Nishihara (1968) developed equations for a set of four models for the adiabatic condensation of water vapour. In developing these equations, however, they used the dry adiabatic equation for the change of volume with temperature, and thus have neglected the latent heat of condensation released. This causes large errors in the amount of water vapour condensed and thus in the change of the oxygen ratio, especially at higher temperatures. To remove this error a saturated-pseudoadiabatic cooling process was used to obtain the change of volume with temperature.

Following Miyake et al. (1968) four models were developed. For models 1 and 2 a closed system was considered, so that all condensed water remained in the system during further cooling. In models 3 and 4 an open system was considered in which most of the condensed water was removed from the system, except that the cloud retained a fixed liquid water density W . It was assumed the the oxygen ratio was a close approximation to the ^{18}O concentration (less than 0.3 per cent error) and thus was used to represent both.

For saturated air, the mass of water vapour, N_V , can be obtained by the expression for the saturated mixing ratio, w_s ,

$$N_V = m w_s = m \frac{\epsilon e_s}{p - e_s} \quad (3.1)$$

where m is the mass of the air under consideration, ϵ is the ratio of the molecular weights of water and dry air ($=0.622$), e_s is the saturated vapour pressure with respect to water, and p is the total pressure. To obtain the saturated vapour pressure, integration of the Clausius - Clapeyron equation for evaporation yields,

$$\ln e_s = - \frac{ML}{R^*T} + \text{constant} \quad (3.2)$$

where M is the molecular weight of water, L is the latent heat of evaporation, and R^* is the universal gas constant. Evaluating Eq. (3.2) at 0 C (considering L to be constant over the atmospheric range of temperature) results in

$$e_s = 6.1078 \exp \left(A + \frac{B}{T} \right) \quad (3.3)$$

where e_s is now the saturated vapour pressure with respect to water, in millibars, 6.1078 is the saturated vapour pressure at 0 C (List, 1966) and the constants A and B are 19.834 and -5417.8, respectively.

For saturated air, using the ideal gas law

$$V = mRT^*/p \quad (3.4)$$

where m is the mass of air, R is the gas constant for dry air, and T^* is the virtual temperature given by ¹

$$T^* = \left(\frac{1 + w_s / \epsilon}{1 + w_s} \right) T \quad (3.5)$$

The fractionation factor α was given by Miyake et al. (1968) in the form

$$\alpha = 1 + c + \frac{d}{T} \quad (3.6)$$

where the constants c and d have values of -0.0105 and 5.8 , respectively.

3.2.1 Model 1

For a closed system, the mass balance equation for ^{18}O is

$$(N_V C_V)_0 = N_V C_V + N_L C_L \quad (3.7)$$

and for the total water substance is

$$(N_V)_0 = N_V + N_L \quad (3.8)$$

where $()_0$ denotes the initial conditions, N is the mass of water substance, C is the oxygen ratio, and subscripts V and L refer to the vapour phase and liquid phase, respectively. If simple equilibrium as given by Eq. (2.3) is considered, then Eqs. (3.7) and (3.8) can be solved to give

$$C_L = \frac{(N_V C_V)_0}{\left(\frac{1}{\alpha} - 1 \right) N_V + (N_V)_0} \quad (3.9)$$

1. The virtual temperature is a factor used in the ideal gas law to correct for the presence of water vapour in the air.

By evaluating N_V and α according to Eqs. (3.1) and (3.6), respectively, the oxygen ratio in the liquid can be calculated during the cooling process.

3.2.2 Model 2

Because this is also a closed system, Eqs. (3.7) and (3.8) remain valid. If Rayleigh condensation is considered, Eq. (2.5) can be integrated to give

$$(C_V)_i = (C_V)_{i-1} \left[(N_V)_i / (N_V)_{i-1} \right]^{\alpha-1} \quad (3.10)$$

where subscripts i and $i-1$ refer to the i th and the preceding condensation steps, respectively. Thus C_V can be determined at each step. Combining Eqs. (3.7) and (3.8)

$$C_L = \frac{(N_V C_V)_o - N_V C_V}{(N_V)_o - N_V} \quad (3.11)$$

and the oxygen ratio in the liquid can be determined during the cooling process.

3.2.3 Model 3

For an open system such that liquid is removed from the system, the conservation of mass equations (Eqs. (3.7) and (3.8)) are no longer valid. Thus an infinitesimal condensation was considered. This small change can be thought of as a closed system, and the equations for the conservation of the oxygen isotope and for the water, written for this small change, become

$$d(N_V C_V) + d(N_L C_L) = 0$$

$$dN_V + dN_L = 0 \quad (3.12)$$

If simple equilibrium is assumed for this change, substitution of Eq. (2.3) and Eq. (3.12) yields

$$N_V dC_V + C_V dN_V = -N_L (C_V d\alpha + \alpha dC_V) + \alpha C_V dN_V$$

or, on rearrangement

$$\frac{dC_V}{C_V} = \frac{(\alpha-1) dN_V - WVd\alpha}{N_V + \alpha WV} \quad (3.13)$$

because W may be defined as N_L / V .

Using a Taylor Series expansion for dN_V and neglecting terms higher than second order

$$\frac{d(N_V)_i}{dT} = \frac{(N_V)_{i+1} - (N_V)_{i-1}}{2\Delta T} \quad (3.14)$$

Denoting this as ΔN , integration of Eq. (3.13) yields

$$(C_V)_i = (C_V)_{i-1} \exp \left[\frac{(\alpha-1)\Delta N + \frac{WVd}{T_i^2} (T_i - T_{i-1})}{N_V + WV\alpha} \right] \quad (3.15)$$

that can be evaluated at each step. By using Eq. (2.3) the oxygen ratio can be calculated as a function of temperature.

3.2.4 Model 4

Assuming Rayleigh condensation for the infinitesimal change, Eq. (2.5) can be rearranged to yield

$$N_V dC_V + C_V dN_V = \alpha C_V dN_V$$

and substituting this into Eq. (3.12) yields

$$\alpha C_V dN_V = -N_L dC_L + C_L dN_V$$

or

$$dC_L = \frac{C_L - \alpha C_V}{N_L} dN_V \quad (3.16)$$

Because Eqs. (3.10) and (3.14) apply

$$\frac{dC_L}{dT} = \frac{C_L - \alpha (C_V)_{i-1} [(N_V)_i / (N_V)_{i-1}]^{\alpha-1} \Delta N}{WV}$$

which can be integrated to give

$$(C_L)_i = \frac{[b + a (C_L)_{i-1}] \exp [a (T_i - T_{i-1})]}{a} - \frac{b}{a} \quad (3.17)$$

$$a = \Delta N / WV$$

where

$$b = -a \alpha (C_V)_{i-1} [(N_V)_i / (N_V)_{i-1}]^{\alpha-1}$$

Thus the oxygen ratio is calculated at different temperatures during the cooling.

For the models, the pressures were obtained from a tephigram for a saturated-pseudoadiabat starting at the 1000mb level and for every -2 C increment in temperature along the curve to a final temperature of -30 C. From Eqs. (3.1) and (3.4) the amount of moisture and the volume, respectively, were obtained for one kilogram of dry air at each pressure-temperature point. These data along with an initial ^{18}O

concentration in the vapour supplied the basic information required for the four models.

3.2.5 Results

To demonstrate the results of the saturated-pseudoadiabatic cooling models described above, water vapour with an oxygen ratio that was in equilibrium with SMOW (a δ value of 0.0) at 20 C was cooled to -28 C in increments of 2 C for each of the models. It was assumed that super-cooled liquid water was the condensed phase for temperatures below freezing.

In Figure 2 is shown the variation of δ values of the water with cooling for models 1 and 2. It should be noted that although the theory of Rayleigh condensation as used in model 2 should cause a greater fractionation than for model 1, the imposition of the closed system that retains the condensate has removed the effect of this fractionation. As has been mentioned, a closed system is not felt to be a realistic approach to the atmosphere.

Figures 3 and 4 show the variation of δ values for models 3 and 4, respectively, assuming liquid water contents (denoted as LWC in the figures) between 2.0 and 0.01 grams per cubic meter. These open system models exhibit much larger fractionations than do the closed system models discussed above. Close examination again reveals that the equilibrium model 3 has a greater fractionation than does the Rayleigh condensation model 4, with the results of the two models converging as the liquid water content decreases towards zero. This is again due to the presence of the liquid water in the system that allows some exchange and thus strictly not Rayleigh conditions that require the immediate

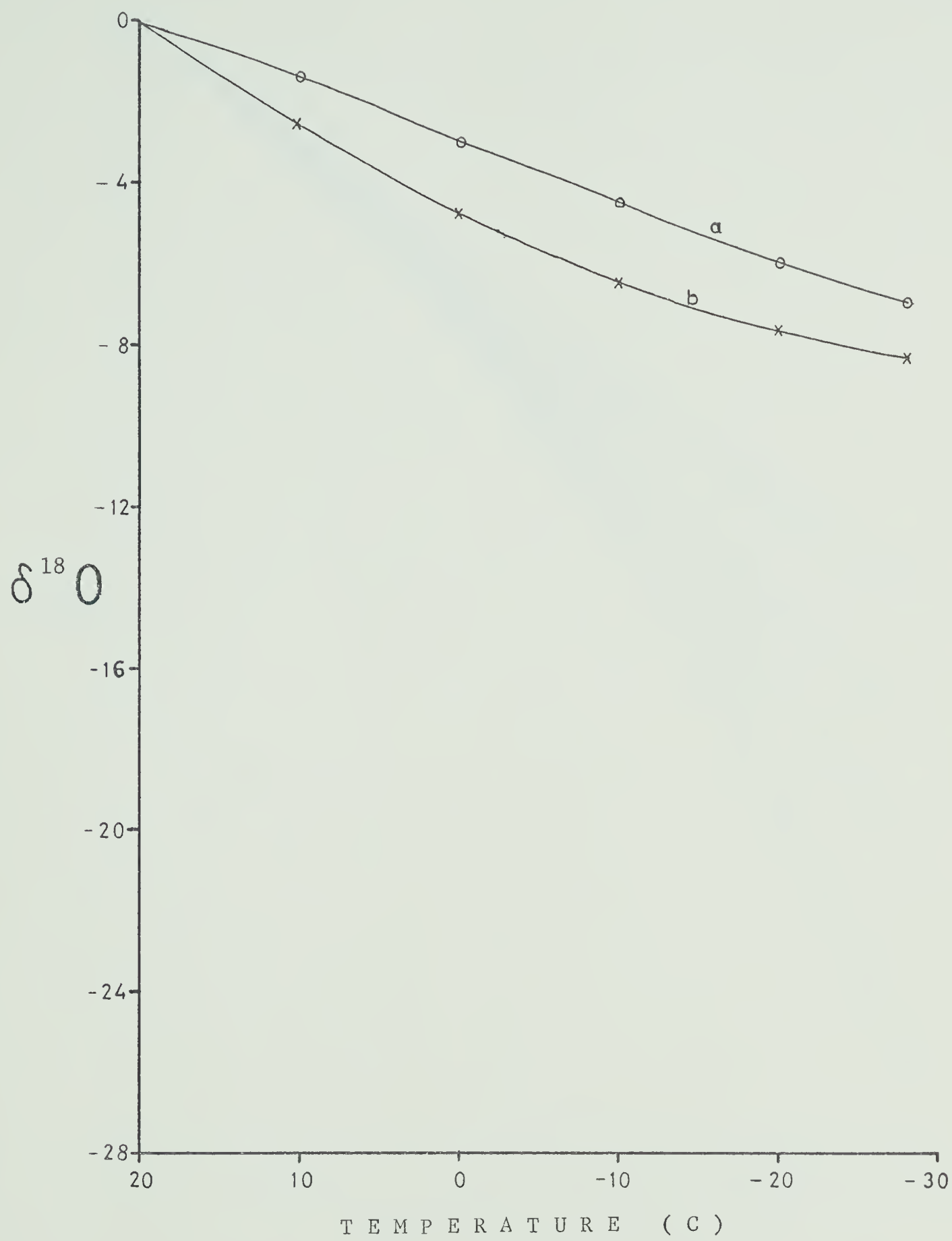


Figure 2. $\delta^{18}O$ values as a function of temperature for pseudo-adiabatic cooling (models 1 and 2). (b) model 1, (a) model 2. Values plotted every 10 degrees (calculated every 2 degrees).

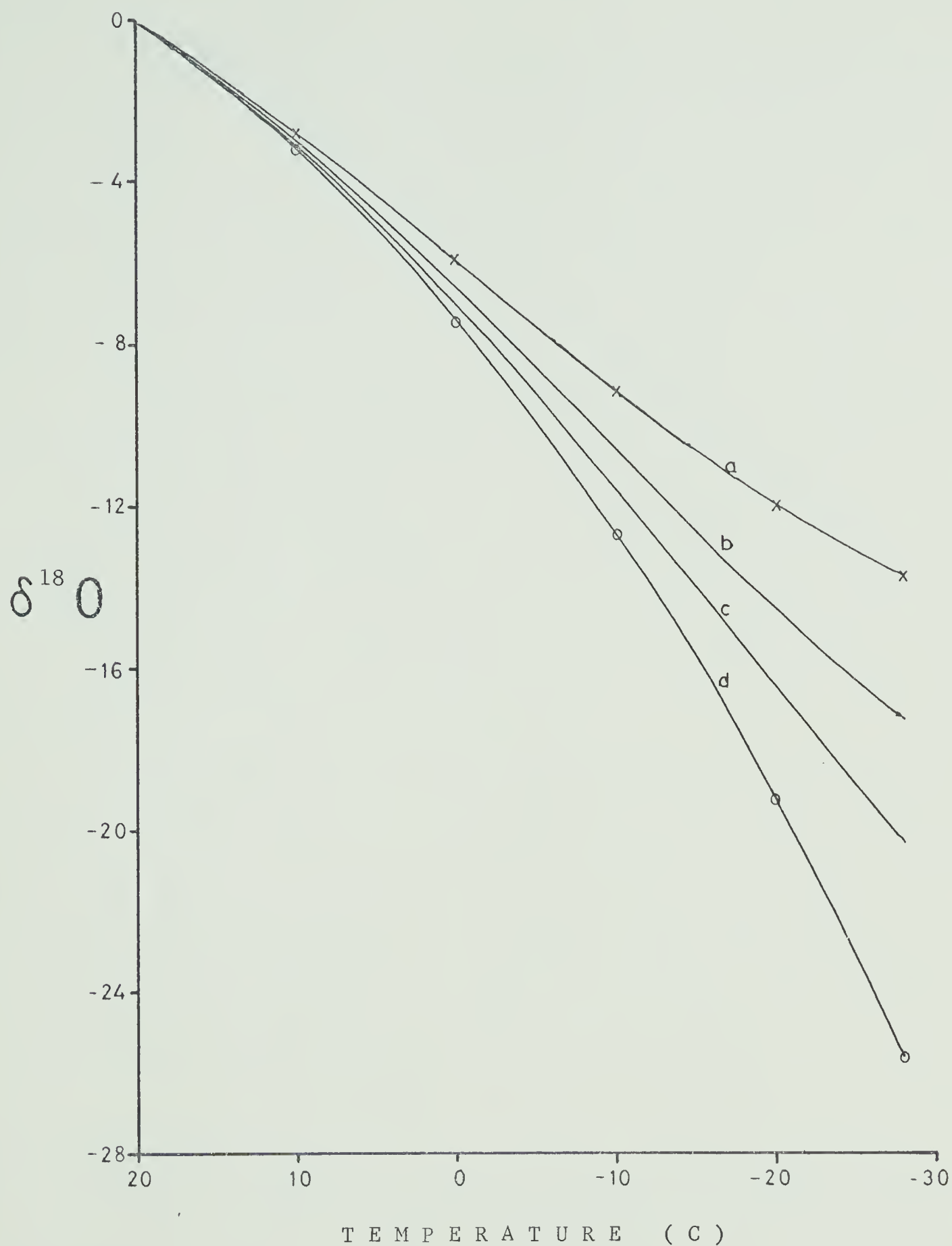


Figure 3. $\delta^{18}O$ values as a function of temperature for pseudo-adiabatic cooling (model 3). LWC of 2.0 (a), 1.0 (b), 0.5 (c), and 0.01 (d).

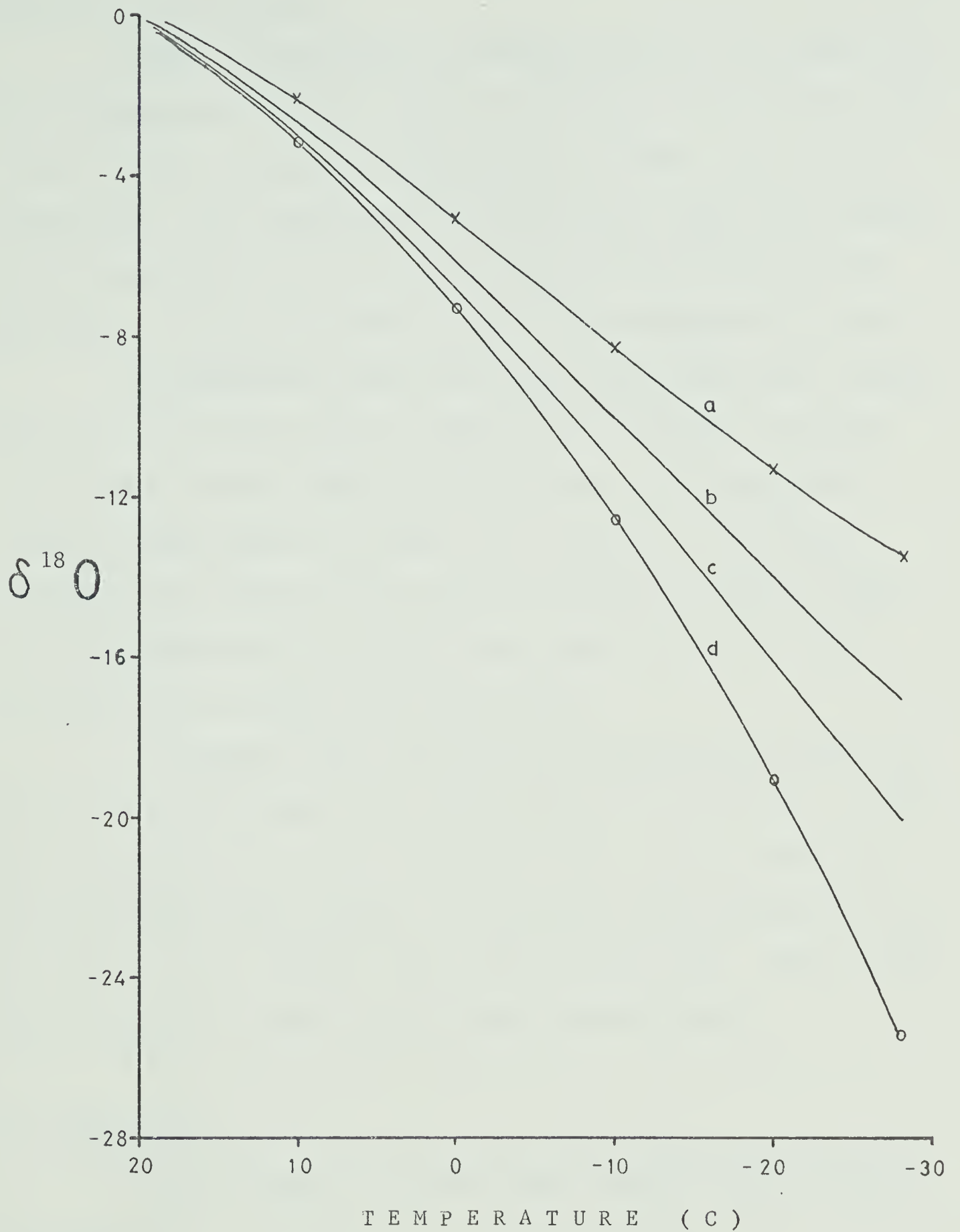


Figure 4. $\delta^{18}O$ values as a function of temperature for pseudo-adiabatic cooling (model 4). LWC of 2.0 (a), 1.0 (b), 0.5 (c), and 0.01 (d).

removal of the condensate.

Figure 5 demonstrates the changes that occur if different initial temperatures are used. Initial temperatures of 30, 20, 10, and 0 C were used with the vapour in equilibrium with SMOW at these initial temperatures. This demonstrates the effect of the latent heat released at the warmer temperatures, resulting in less fractionation for the same change in temperature when a higher initial temperature is used.

To demonstrate further the effect of the latent heat released during cooling Figure 6 shows a comparison of results of the models derived above (the wet models) with the results that were obtained using the models derived by Miyake et al. (1968) (the dry models). The same initial conditions were used for both sets of models, namely an initial temperature of 30 C and water vapour with an ^{18}O content in equilibrium with SMOW at that temperature.

For models 1 and 2 the wet models exhibited δel values that were up to 1.2 ppt greater than those given by the dry models, a change of over twenty-five per cent. In models 3 and 4 the wet models give final δel values that were over 5.0 ppt greater than those given by the dry models, again a change of over twenty-five per cent. Other liquid water contents for models 3 and 4 showed similar results.

3.3 Evaporation

For an evaporating raindrop Kinzer and Gunn (1951) developed the equation

$$\frac{dM}{dt} = 4\pi r D(\rho_a - \rho_b) \theta \quad (3.18)$$

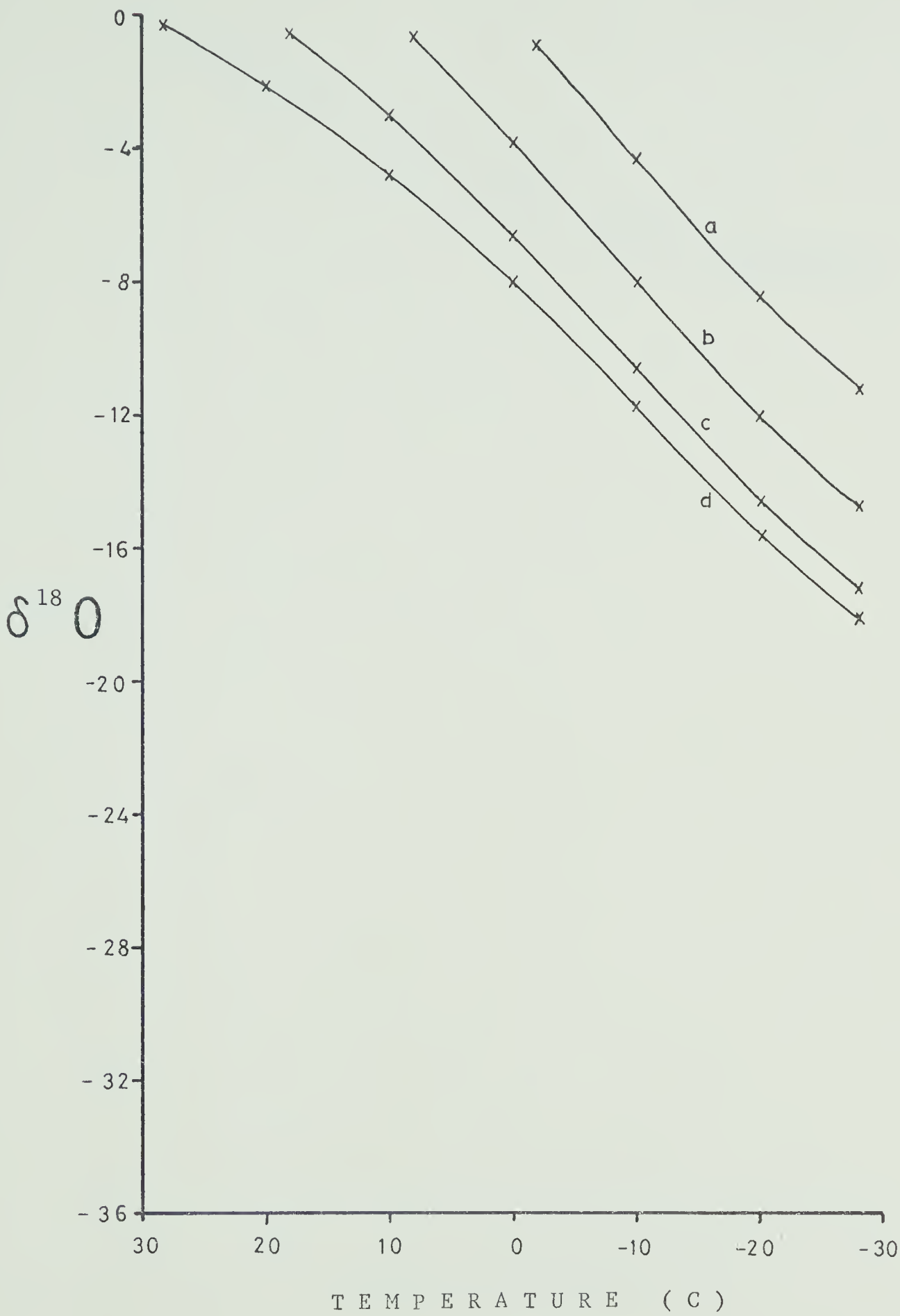


Figure 5. The effect of changing the initial temperature for model 3. Initial temperatures of 0 C (a), 10 C (b), 20 C (c), and 30 C (d). LWC of 1.0 .

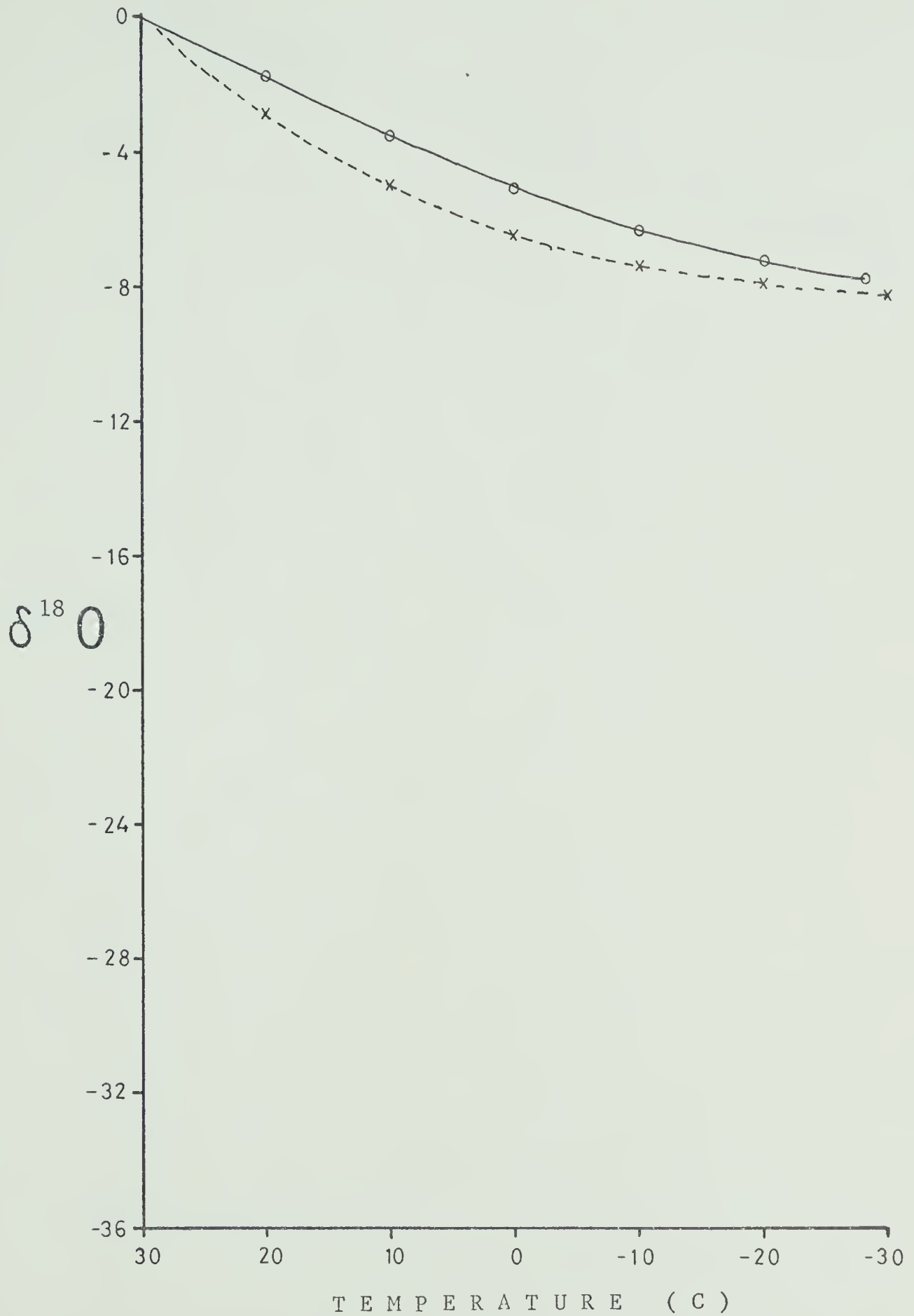


Figure 6a. A comparison of the wet models to the dry models during cooling. Solid line is for the wet models, dashed line is for the dry models. Model 1.

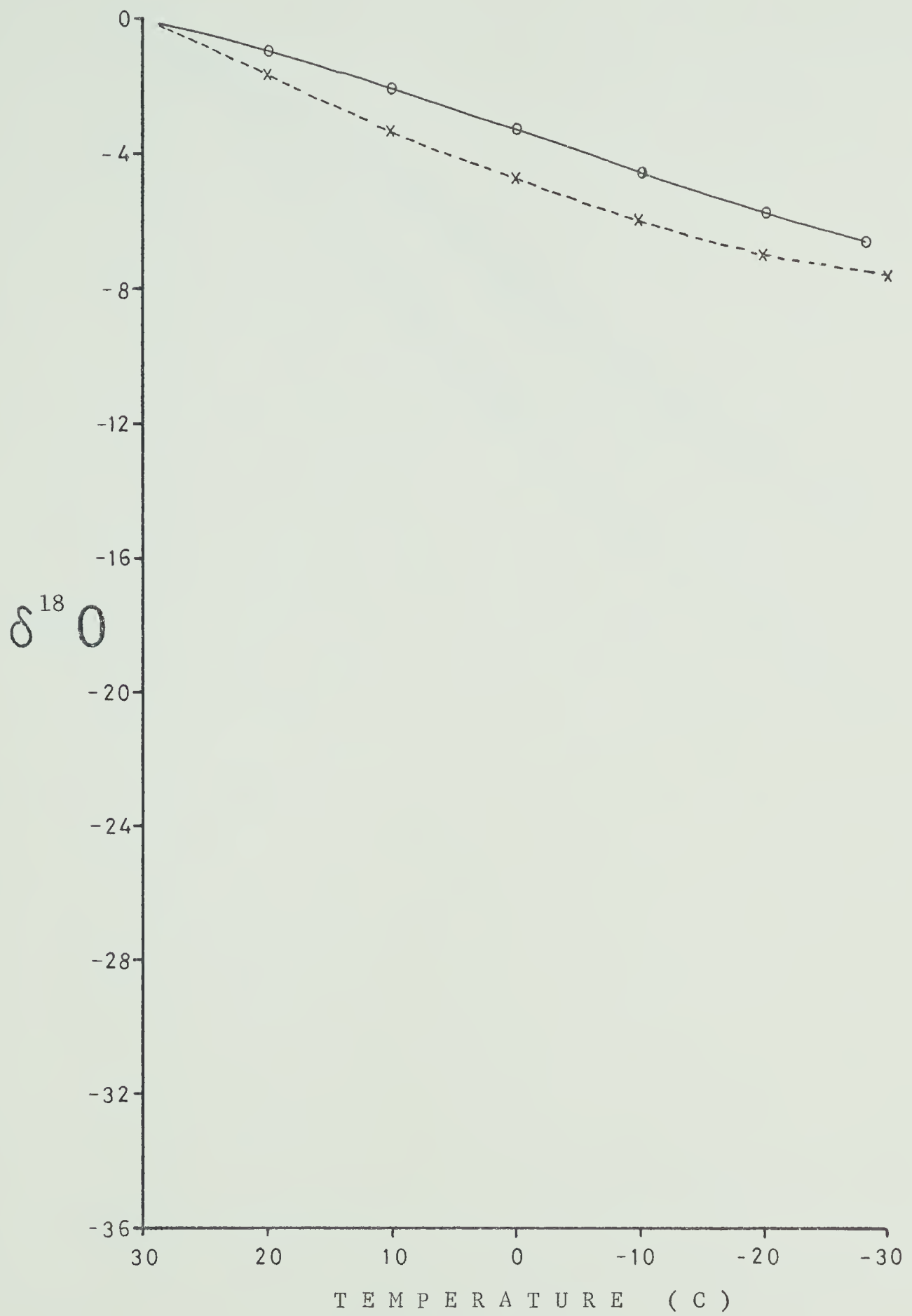


Figure 6b. Model 2.

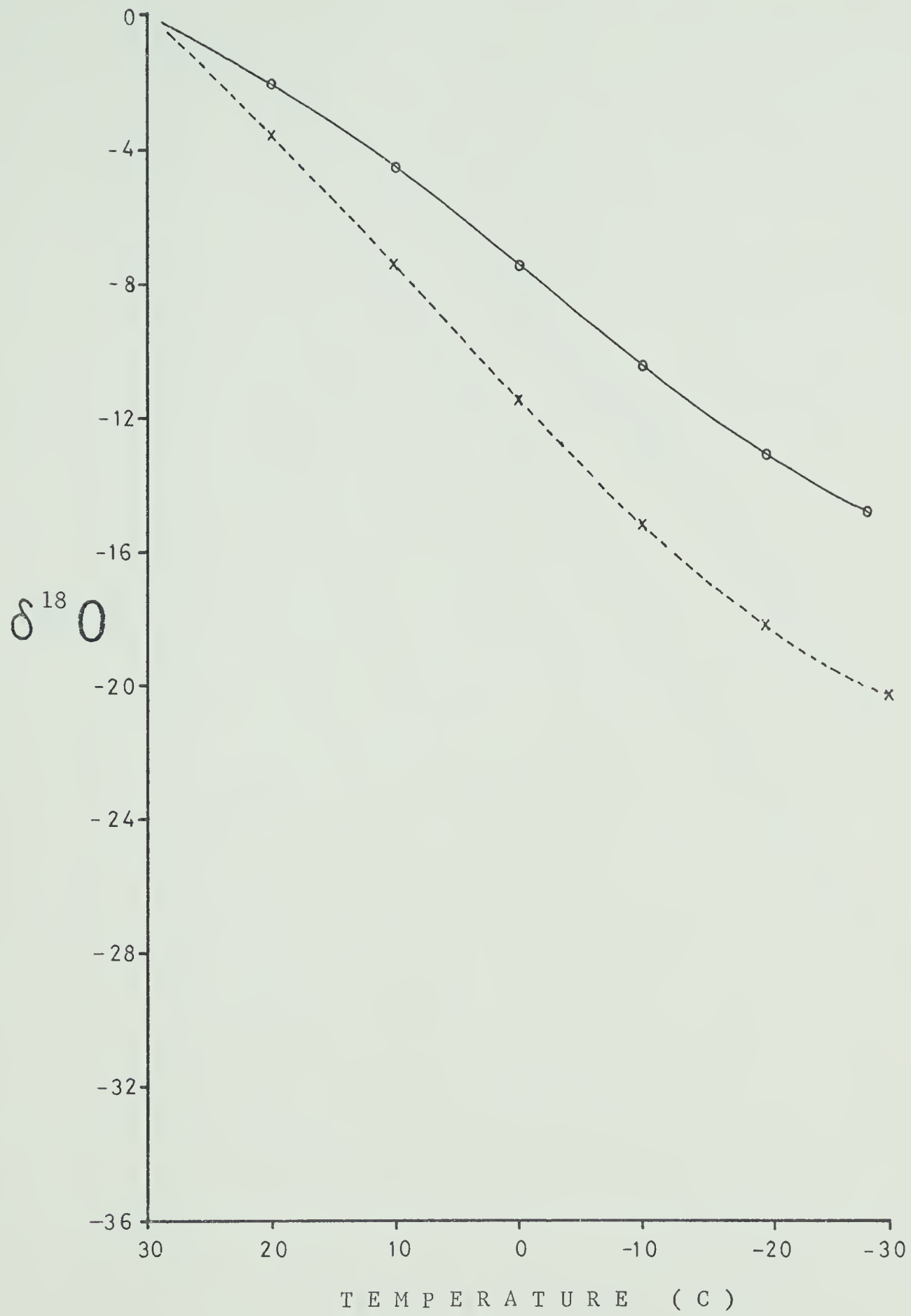


Figure 6c. Model 3. LWC of 2.0

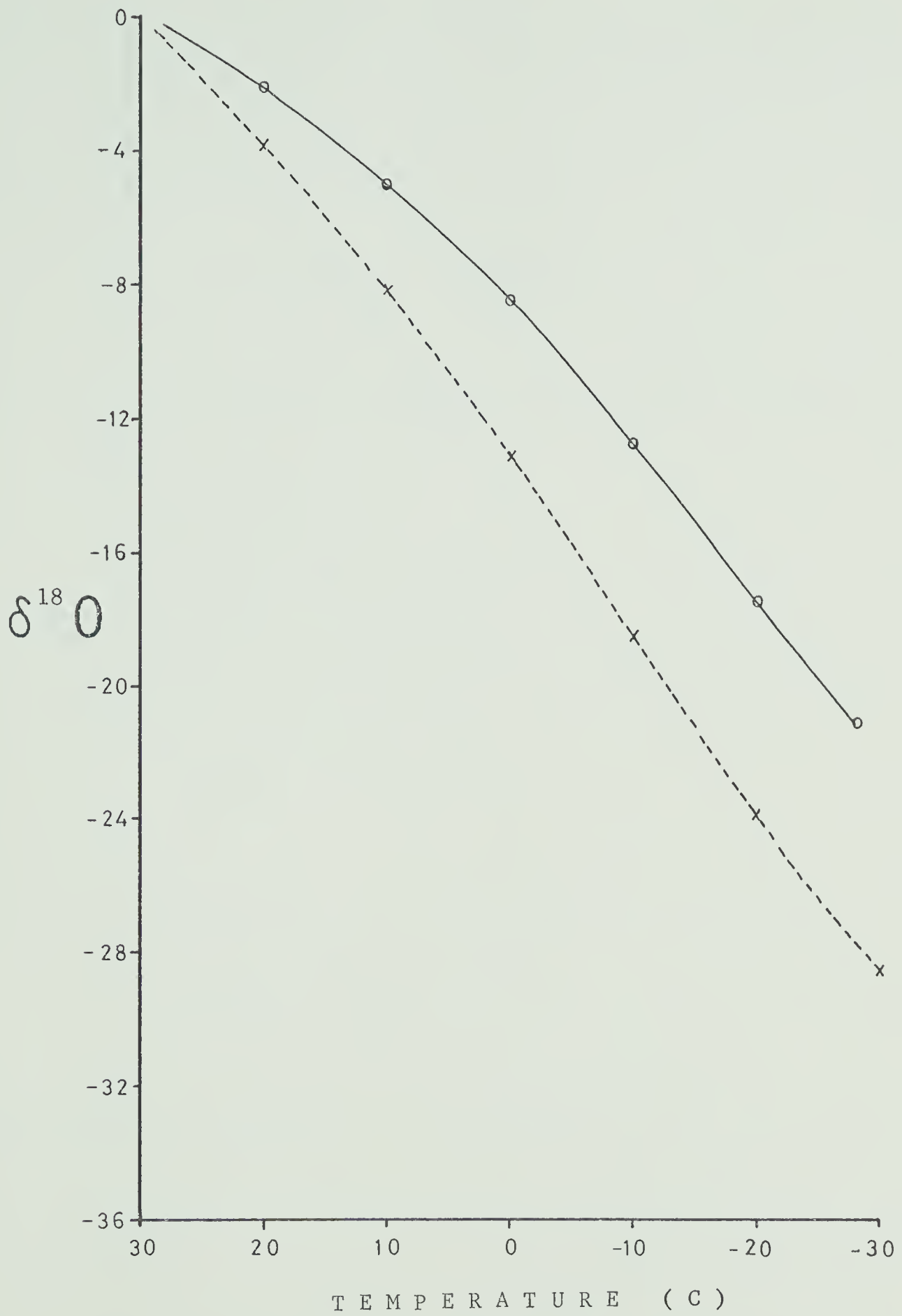


Figure 6d. Model 3. LWC of 0.5

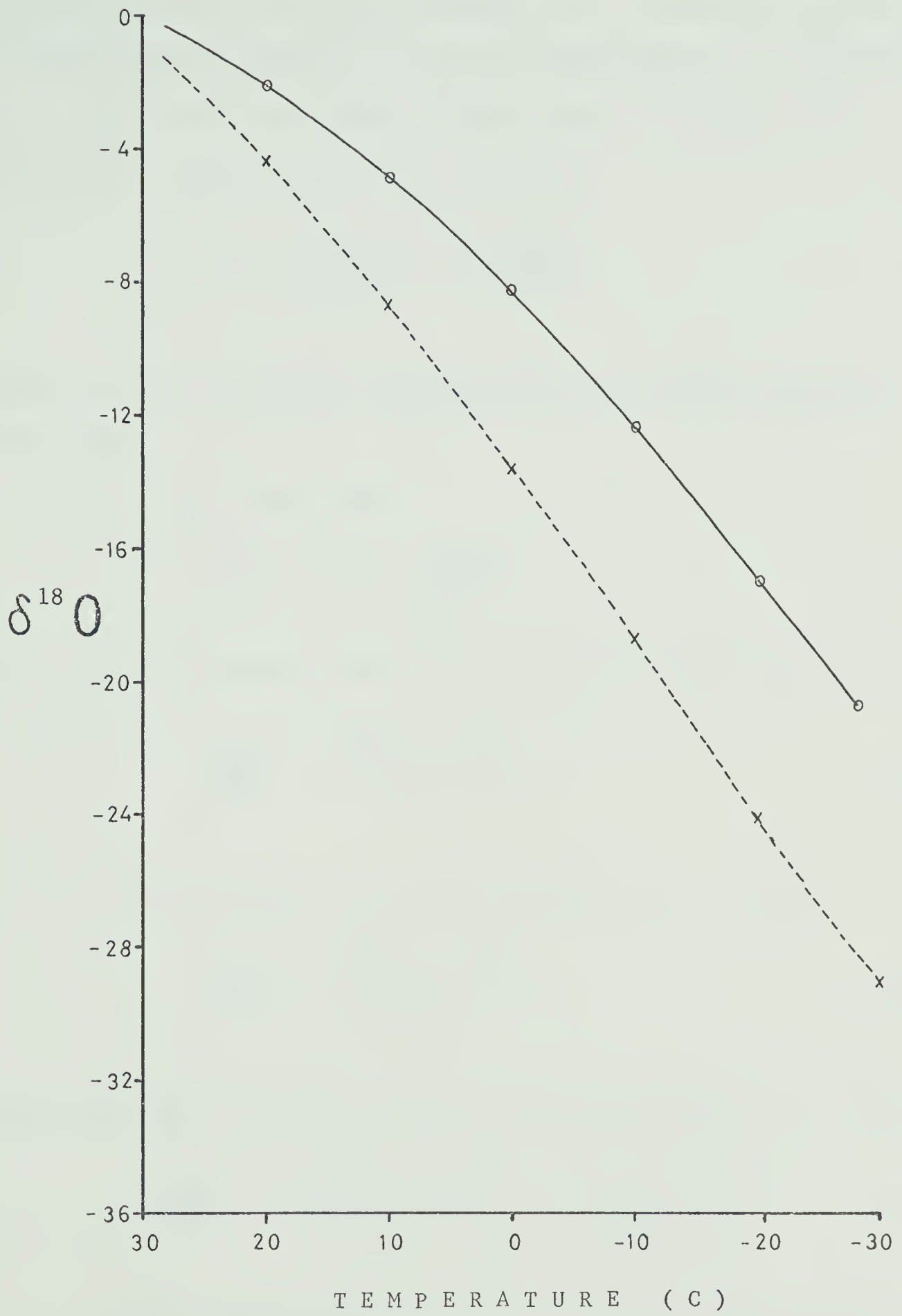


Figure 6e. Model 4. LWC of 0.5

where M is the mass of a drop of radius r , ρ is the vapour density at the drop surface (subscript a) and in the environmental air (subscript b), θ is the ventilation factor defined in Eq. (2.12) and D is the diffusivity of water vapour in air, given by

$$D = D_o \left(\frac{T}{T_o} \right)^{1.81} \left(\frac{1000}{p} \right)$$

where D_o is the diffusivity at temperature T_o and 1000 mb pressure (List, 1966).

It can be shown that

$$\frac{dM}{dt} = 2\pi r \rho_w \frac{d(r^2)}{dt}$$

where ρ_w is the density of the water drop, and thus Eq. (3.18) becomes

$$\frac{d(r^2)}{dt} = \frac{2D (\rho_a - \rho_b)}{\rho_w} \theta \quad (3.19)$$

and for a drop falling at its terminal velocity V_r ($= dz/dt$)

$$\frac{d(r^2)}{dz} = \frac{2D (\rho_a - \rho_b)}{V_r \rho_w} \theta \quad (3.20)$$

Substituting Eq. (2.12) for θ in Eq. (3.20) and expanding $Re = 2rV_r/\nu$

$$\frac{d(r^2)}{dz} = \frac{2D (\rho_a - \rho_b)}{V_r \rho_w} \left[1 + F \left(\frac{r V_r}{2\pi D} \right)^{1/2} \right] \quad (3.21)$$

Using a Taylor Series expansion for $r(z - \Delta z)$ and neglecting second order and higher terms

$$r_i^2 = r_{i-1}^2 - \frac{d(r^2)}{dz} \Delta z \quad (3.22)$$

In order to use Eq. (3.21) it was assumed that the temperature of the drop was equal to the wetbulb temperature of the air. The terminal velocities were calculated using Eq. (4) of Wobus, Murray, and Koenig (1971). This equation gives an empirical fit to the terminal velocities determined by Gunn and Kinzer (1949) with less than 0.5 per cent error for radii larger than 50 microns. These velocities were modified according to Eq. (7) of Wobus et al. (1971) for conditions other than a pressure of 1013.25 mb, a temperature of 20 C, and a relative humidity of 50 per cent. Wobus et al. (1971) state that this adjustment gives terminal velocities up to 10 per cent larger than those measured.

Using the results of Eq. (3.22) considering different environments, the oxygen ratio of the evaporating drop was calculated using Eq. (2.6). Eqs. (3.6) and (2.8) were used to calculate the fractionation factor for equilibrium and kinetic effects, respectively.

3.3.1 Results

To demonstrate the effect of evaporation, a cloud based at 1375 meters above the ground was chosen. The surface temperature was 26 C with a dry adiabatic lapse rate to the cloud base. The relative humidity was 46.6 per cent at the ground and increased linearly to 100 per cent at the cloud base. The water vapour below cloud base had a δ value that was in equilibrium with water with a δ value of -10.0 ppt at 20 C.

Under these conditions Figure 7 shows how the δ values of the raindrops changed with height, based on an initial δ value of -13.2 ppt for the drops and with equilibrium evaporation conditions. This demonstrates how the evaporation effect increases with decreasing

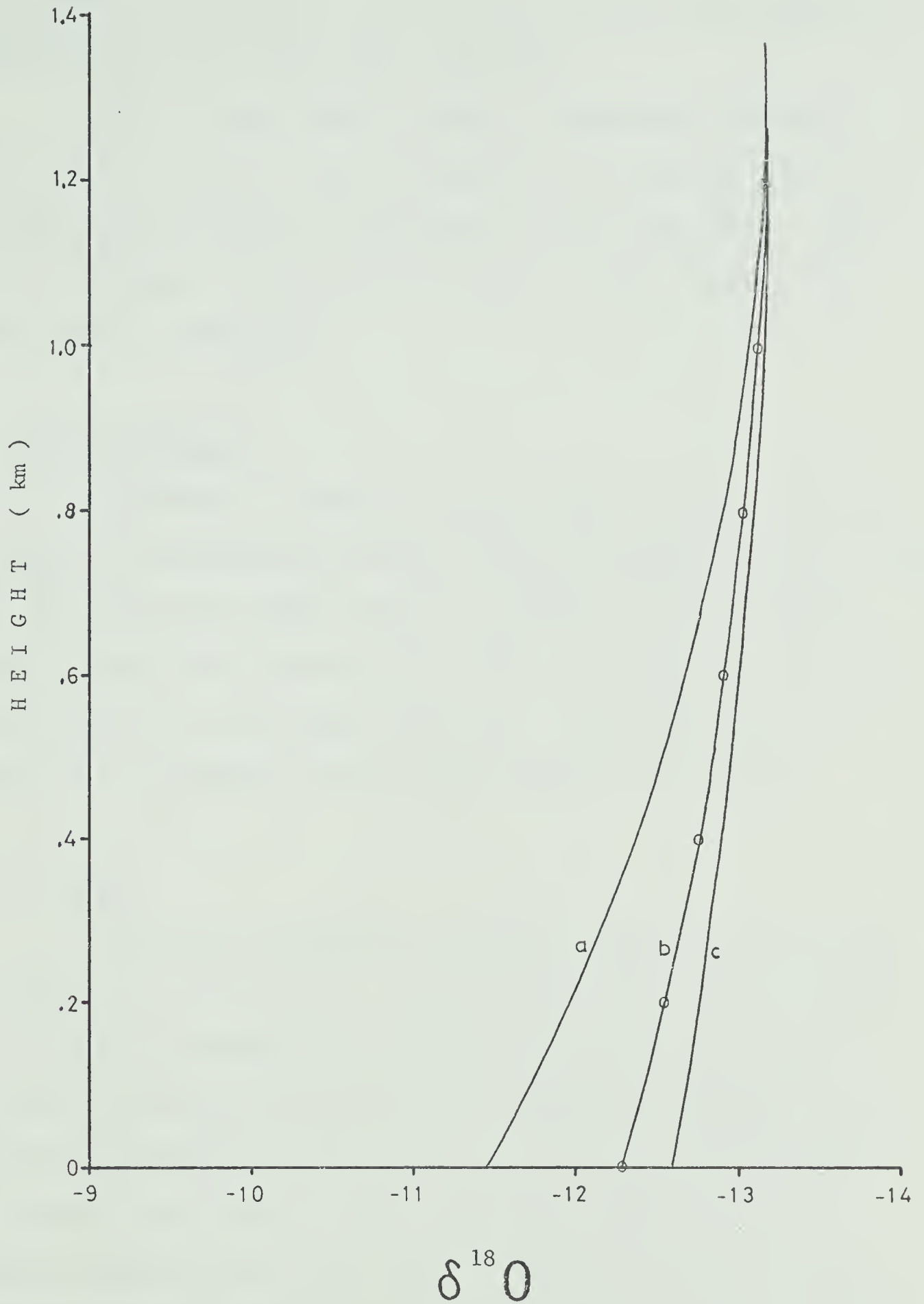


Figure 7. The variation of $\delta^{18}O$ values of raindrops during descent for equilibrium evaporation. Initial $\delta^{18}O$ value of -13.2. Drop radii of 1.0 mm (a), 1.6 mm (b), and 2.5 mm (c).

drop radius and decreasing relative humidity, with a total change of from 0.6 to 1.7 ppt for the drops considered.

Figure 8 shows that the effect of evaporation on the δ values is more marked if kinetic evaporation is considered, even for the high relative humidities experienced near the cloud base. There were total changes of from 1.6 to 3.7 ppt in the δ values of the drops that were considered.

3.4 Exchange Effects

The effect of isotopic exchange between the drop and the environment on the oxygen ratio of the drop was calculated using Eq. (2.10) with the initial drop oxygen ratio as m_i and with an environmental liquid concentration as given by Eq. (2.3) evaluated at the drop temperature from the vapour oxygen ratio as m_f . The elapsed time t is given by $t = z/V_r$ where z is the distance fallen at velocity V_r .

3.4.1 Results

Equilibrium exchange was considered with the same conditions as described in section 3.3.1. Figure 9 shows the effect of exchange. It is noted that exchange had a greater effect at the beginning of the process than near the end, due to the exponential approach to an equilibrium condition with the vapour. This is much more noticeable for a smaller drop (curve a) than for a larger drop (curve c). It should be noted that the total change is greater than that for equilibrium evaporation (Figure 7) but less than that for kinetic evaporation (Figure 8), with final changes of from 1.3 to 2.6 ppt for the drops considered. Of course the magnitude of the effect is dependent upon the amount of disequilibrium between the drops and the vapour.

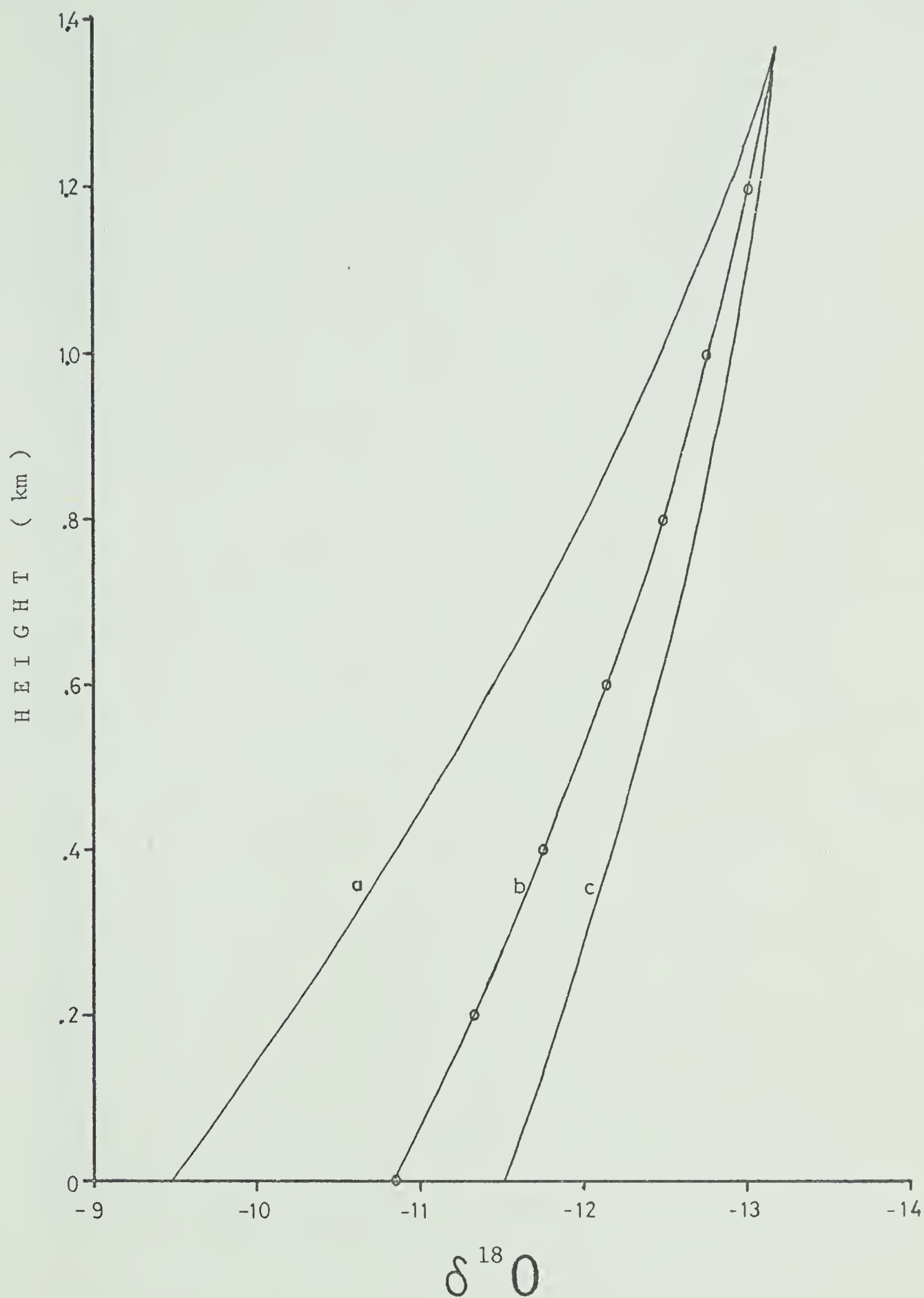


Figure 8. The variation of $\delta^{18}O$ values of raindrops during descent for kinetic evaporation. Lines as for Figure 7.

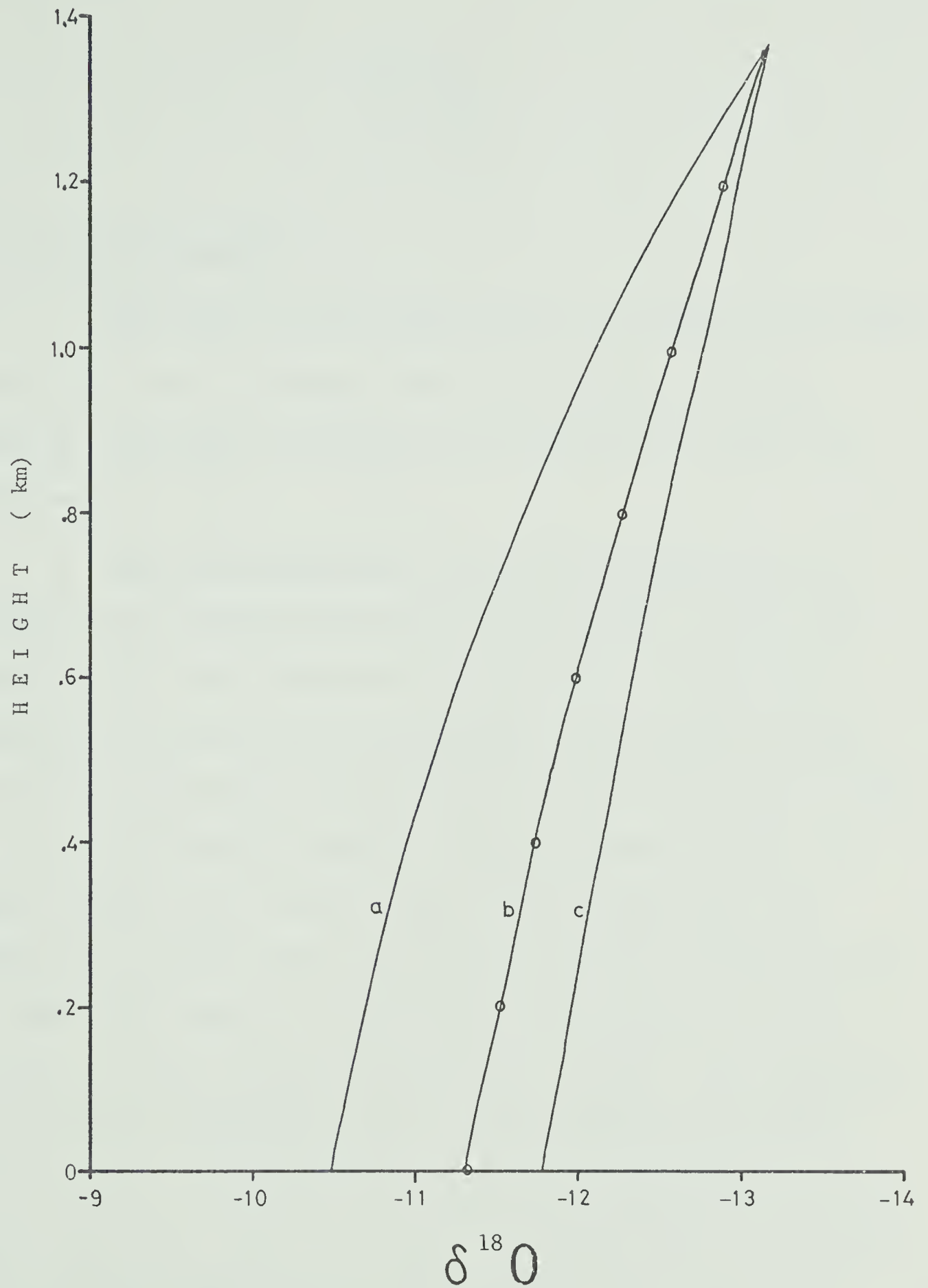


Figure 9. The variation of $\delta^{18}O$ values of raindrops during descent for equilibrium exchange. Lines as for Figure 7. Vapour in equilibrium with water having a $\delta^{18}O$ value of -10.0 at 20 C.

CHAPTER IV

THE DATA

4.1 Collection Methods

The samples used for this study were collected in the period from June, 1970 to September, 1971 in the vicinity of Edmonton, Alberta. There were approximately the same number of samples for each year.

The rain samples were collected in open pans that were placed in well exposed areas during periods of rain. The pan was emptied into a sample bottle that was then closed. Most samples consisted of approximately 40 milliliters except when the rain was too brief in duration or too light in intensity to yield this volume, so that smaller samples resulted. In some instances (during very light intensity rain or when using a small collection pan) the sample was collected over a long period of time in an attempt to get a large enough sample. In these cases some evaporation from the sample could have occurred before it was collected. This evaporation would cause an enrichment of the ^{18}O concentration in the sample. Also with the long sampling times equilibrium exchange with the water vapour in the air could have modified the oxygen ratio of the sample if it differed significantly from the oxygen ratio of the vapour.

The snow (hail) samples were collected from areas of newly-fallen snow (hail) and were placed in sealed containers before being allowed to melt. The melt-water was then transferred to a sample

bottle to be kept for analysis.

The temperature data were extracted from thermograph records of a mesometeorological network in the city of Edmonton. The temperatures recorded were averaged over the period of the sample collection. The temperature data have a probable error of ± 1.0 C considering all sources of error.

4.2 Analysis Method

The samples were prepared for analysis on the mass spectrometer by the standard method as given by Epstein and Mayeda (1953). This process involves equilibration of the water sample with carbon dioxide of a known ^{18}O content under prescribed conditions. The modified carbon dioxide was then analysed on the mass spectrometer² by comparing its oxygen ratio to that of the standard carbon dioxide.

The preparation of the sample for equilibration was carried out in a very low pressure (approximately 10^{-5} mm of Hg.) system. Three times during this process the water sample was frozen to very low temperatures (less than -140 C) and then was exposed to the near vacuum. If on any of these occasions, especially the first when freezing was accomplished with the sample at atmospheric pressure, the sample was not completely frozen, evaporation of some of the sample would have occurred. This evaporation would have led to a slight ^{18}O enrichment of the sample.

² Analyses on the mass spectrometer were carried out in collaboration with the Department of Physics, University of Alberta.

Figure 10 shows a listing of the computer output produced during analysis of one sample.³ The numbers 2**7 and 2**2 specify that 128 consecutive readings were averaged to produce each reading printed and that an average of 4 readings was used to calculate each trial value, respectively. Four trials of both the standard (S) and the sample (X) were run. Then the ratio of the sample value to the standard value (X/S ratio) was computed. For this calculation one of two alternate methods was used. If a central sample value was considered it was divided by the mean of the two standard values that surrounded it. If a central standard value was considered it was divided into the mean of the two sample values that surrounded it. The two methods were used alternately for the six central values and thus six ratios were computed and printed, along with the mean value and the standard deviation of the ratios. If the standard deviation was greater than 0.0002 (0.2 ppt), one or two X/S ratios could be deleted from the set of six if they appeared to be in obvious disagreement and the mean and standard deviation were recalculated. If the standard deviation remained too large another three trials were performed and a new mean X/S ratio and standard deviation were calculated. This procedure produced an X/S ratio (and thus del value by Eqs. (2.1) and (2.2)) with a standard deviation of 0.2 ppt.

This measured del value was, strictly speaking, for the

³ Computer program was written by R. N. Hunt of the Department of Physics.

INTTME=2**7

GMTIME=2**2

FIRST SET MUST BE S !

THIS SET IS S

00.39788	00.39786	00.39779	00.39776
----------	----------	----------	----------

00.39782 S

THIS SET IS X

00.40006	00.40010	00.40009	00.40016
----------	----------	----------	----------

00.40010 X

THIS SET IS S

00.39810	00.39799	00.39802	00.39814
----------	----------	----------	----------

00.39806 S

THIS SET IS X

00.40017	00.40026	00.40019	00.40023
----------	----------	----------	----------

00.40021 X

THIS SET IS S

00.39812	00.39818	00.39815	00.39835
----------	----------	----------	----------

00.39820 S

THIS SET IS X

00.40032	00.40046	00.40047	00.40050
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00.40044 X

THIS SET IS S

00.39843	00.39845	00.39848	00.39852
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00.39847 S

THIS SET IS X

00.40072	00.40059	00.40063	00.40070
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00.40066 X

01.00542	01.00526	01.00522	01.00533	01.00528	01.00521
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MEAN RATIO 01.00528

STD DEV IS 00.00008

TYPE Y IF DEV SATISFACTORY? Y

Figure 10. A sample of the computer output for the analysis of a sample.

carbon dioxide that was equilibrated with the samples. Craig (1957, pp 144-145) gave the correction factor to relate this measured δ value to the actual δ value of the water sample. However, because the measured δ values were small and the correction factor is near unity, the measured δ value was assumed to be that of the water sample (less than 4 per cent error). (See Appendix B for a sample calculation of this correction.)

Table A-1 in Appendix A gives a listing of all the samples that were collected. This includes the δ values of the sample, the air temperature, the δ value of the standard used, the X/S ratio measured, and the location of the collection site.

CHAPTER V

DISCUSSION AND RESULTS

5.1 Introduction

In discussing the results of analysis of the precipitation data collected, only the summer period (the months of May through September) will be considered. Furthermore, only those samples for which surface air temperature observations were available were included.

The data were grouped by month and monthly means of temperature and del value were calculated. Table 1 lists the number of samples in each month, the mean surface air temperature, and the mean del value and standard deviation for each month.

Figure 11 shows these means plotted and includes the straight line of Eq. (1.1) from Dansgaard (1964). As in Figure 1 all mean del values fall below those given by Eq. (1.1) as would be expected.

5.2 General Results

In Chapter I several causes for a variation in del value in precipitation were given. Some implications from these will now be developed.

As can be seen in Figures 1 and 11 and in Table 1 the mean del values for precipitation in the area of interest were near -16 ppt for the summer months. Thus if this water was the source of water vapour for the precipitation and assuming equilibrium evaporation and condensation processes, the first condensate would have had a del value of near -16 ppt and further condensation would have yielded lower del values and the raindrops in the cloud would have had a del value slightly lower than -16 ppt. As shown in Chapter III exchange and evaporation

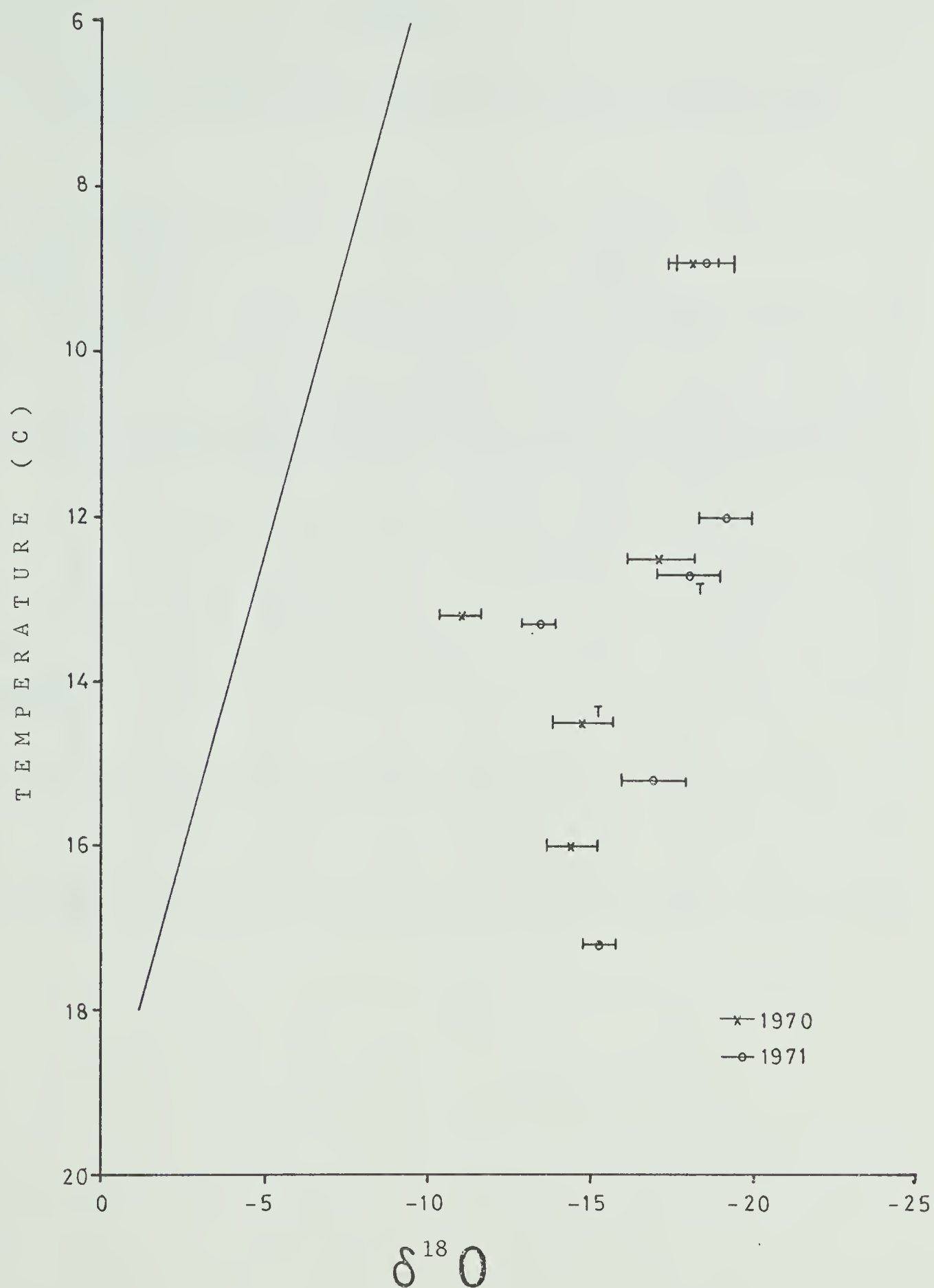


Figure 11. Mean monthly $\delta^{18}O$ values versus mean temperature for the collected samples. Horizontal bars indicate one standard deviation about the mean. Line is Eq. (1.1). Samples marked 'T' are summer means.

TABLE 1

A summary of the samples collected during the summer months

YEAR MONTH	1970				1971			
	NO	\bar{T}	$\bar{\delta}$ ppt	σ ppt	NO	\bar{T}	$\bar{\delta}$ ppt	σ ppt
MAY	0	-	-	-	6	13.3	-13.4	0.9
JUNE	3	8.9	-18.3	2.1	44	12.0	-19.1	1.6
JULY	29	16.0	-14.4	1.6	13	15.2	-16.9	1.8
AUGUST	9	12.5	-17.1	2.0	3	17.2	-15.2	1.1
SEPTEMBER	7	13.2	-11.0	1.5	4	8.9	-18.5	1.6
TOTAL	48	14.5	-14.7	1.8	70	12.7	-18.0	1.8

would have raised this value so that the precipitation would have had a δ value of near -16 ppt. Also as will be shown below (section 5.4) evapotranspiration raises the initial δ value of the vapour and thus of the precipitation. This local evaporation is most marked for convective precipitation.

Another possible large source of the water vapour for precipitation was the Pacific Ocean. It may be considered to have a δ value of near 0 ppt. Thus for equilibrium evaporation and condensation the first condensate would have had a δ value of near zero. Thus the raindrops would have higher δ values than those considered above. However, to get to the area of interest this moisture must have crossed the mountain barrier between the ocean and Alberta. During this traverse of the mountains some of the moisture will have precipitated out and thus only part of the original water vapour comes across the barrier.

As ^{18}O is preferentially condensed out due to the fractionation, this precipitation on the mountains preferentially removed part of the ^{18}O . Thus when the remaining water vapour reached Alberta it was depleted in ^{18}O with respect to its original content and thus further precipitation in Alberta would have had δ values such as those measured. This preferential loss of ^{18}O through precipitation may be regarded as a reservoir effect. Further changes during movement across the mountains can be caused by the mode of transport as described in detail by Eriksson (1965).

5.3 The Change in δ Values with Time

An alternate method of examining the data was to consider the change in δ values with time during a period of precipitation.

In the data collected there were ten different sets that included at least five sequential samples. Each of these sets was then plotted.

5.3.1 Instability Precipitation

Figure 12 shows the change of del values with time that occurred for an airmass type thunderstorm. It was noted that del values decreased with time, with a change of near five ppt. There are several possible explanations for this effect.

One possibility is the effect of exchange and evaporation. At the beginning of the storm the air below the storm would have been much drier and the cloud base higher than near the end of the storm. Thus evaporation of the raindrops would have been much more marked at the initial stages and raised the del values of the initial time and thus the del values would have decreased with time. The effect of exchange would be similar.

A second possibility is the reservoir effect that was described in the previous section (5.2). This would have caused a general decrease of the del values with time as the cloud became depleted in water vapour. A further explanation, the one that the author believes was the most probable, will be explained in detail in the following section (5.4) .

In Figure 13 is shown the change in del values that occurred with a thunderstorm associated with an upper level disturbance that released the instability, rather than surface heating having released the instability. It is immediately noted that there was no general decrease with time of the del values as was noticed in the airmass thunderstorm. If it is assumed that little surface air was drawn into

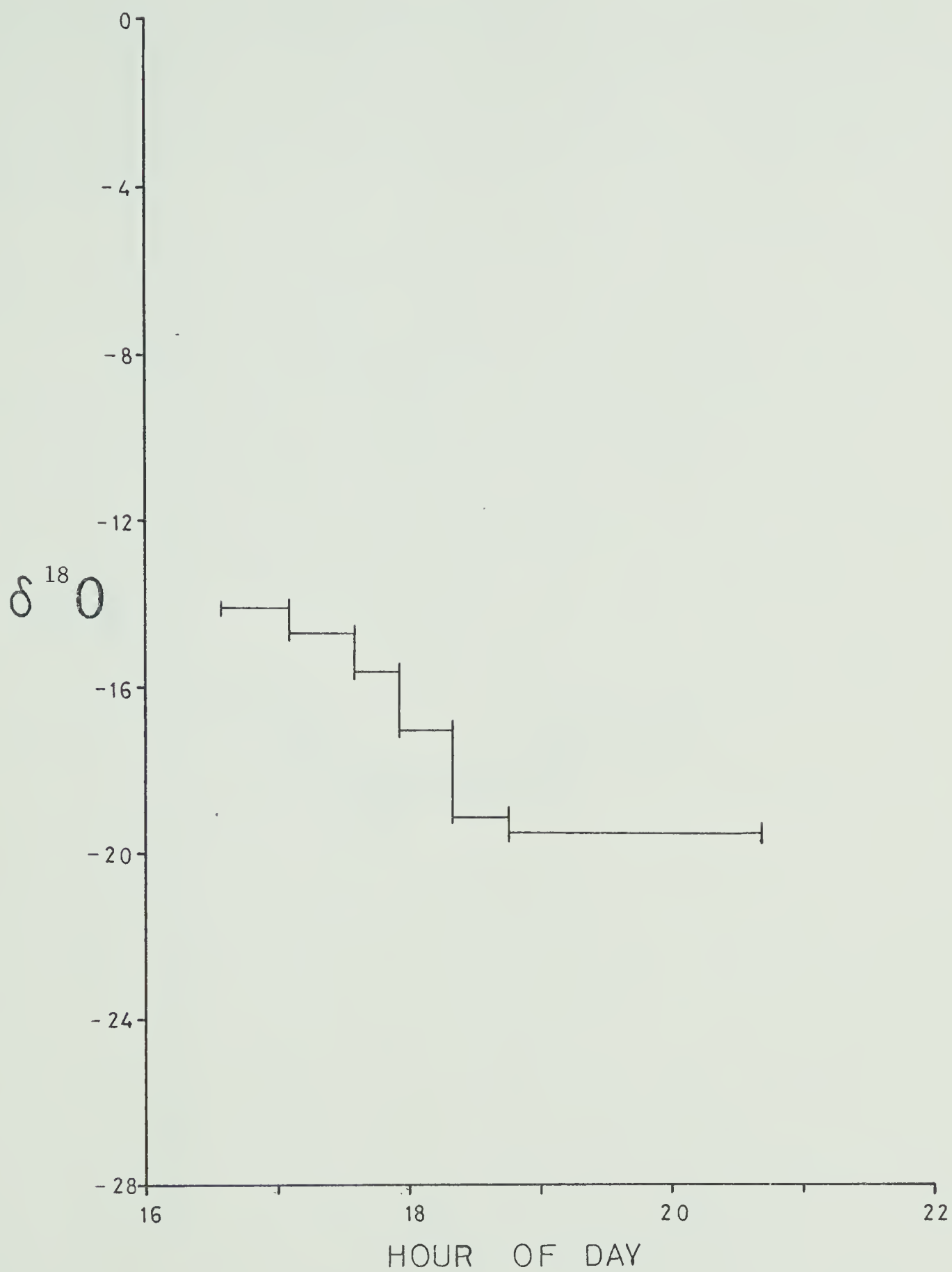


Figure 12. Time variations in $\delta^{18}O$ values of precipitation associated with an airmass thunderstorm on July 23, 1971. Vertical barbs on lines show one standard deviation for measured $\delta^{18}O$ values.

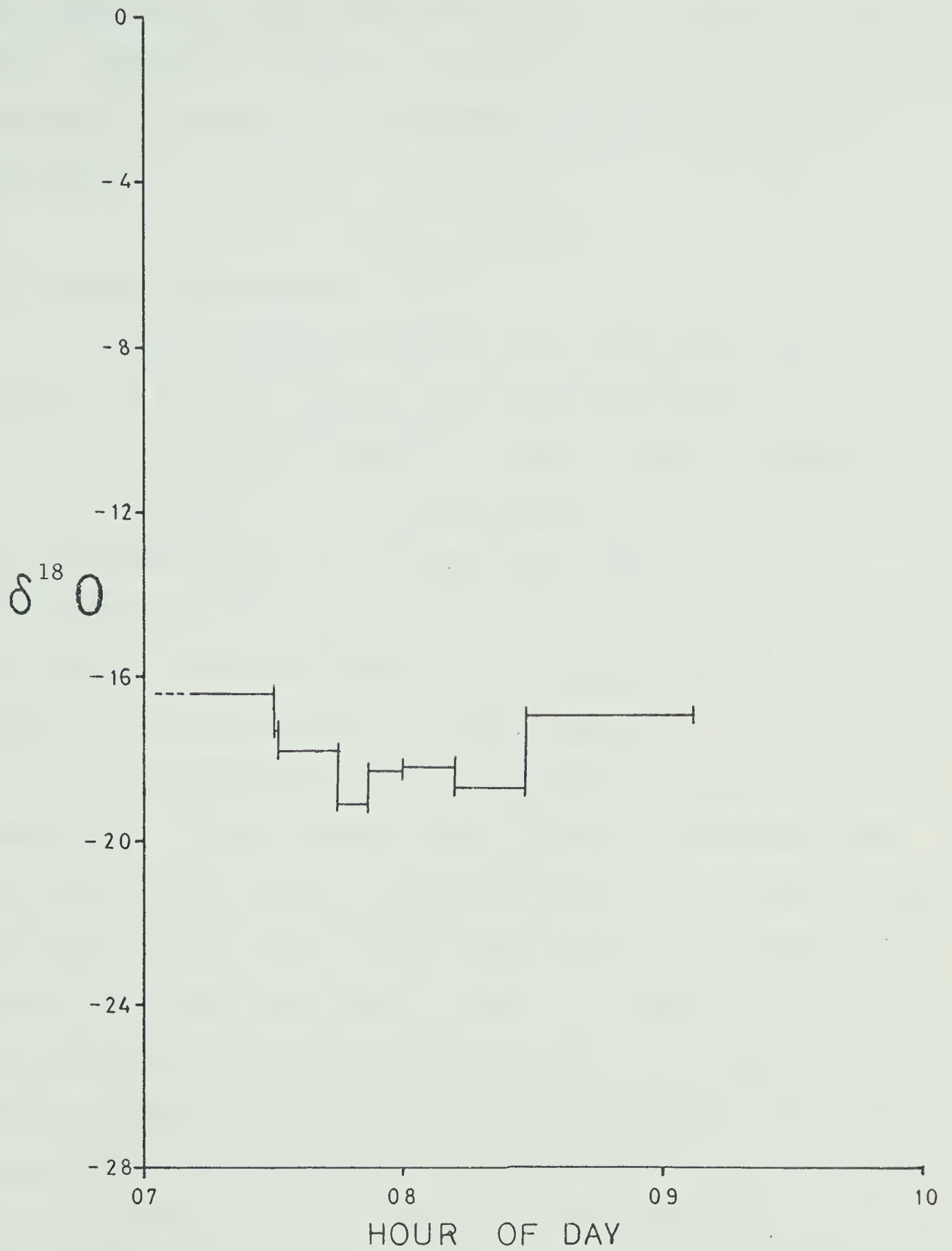


Figure 13. Time variations in $\delta^{18}O$ values of precipitation associated with a non-airmass thunderstorm on August 13, 1970.

the thunderstorm the effect described in Section 5.4 would have been absent. The higher del values at the beginning and the end of the storm were due possibly to the evaporation effect as was described previously.

5.3.2 General Precipitation

Figure 14 shows the change in del values with time that occurred in a synoptic situation that produced warm frontal rain. As the front did not move appreciably towards the area of interest, the general increase in del values attributable to a type of reservoir effect (Dansgaard, 1953) did not take place. Rather the decrease that was evident at the beginning of the observations can be attributed to evaporation effects that decrease with time as the cooler airmass beneath the warm air became more and more saturated.

Figures 15 or 16 show the results for cold-low type of precipitation. Figure 15 shows nearly constant del values with time as there existed no transitory effects to cause the del values to change. The almost continual rain situation shown in Figure 16 also shows near constant del values over a period of days. The higher del value during the daylight hours on the 15th was probably due to an evaporation effect, both of the drops as they fell and of the partial sample in the collection pan because the precipitation at this time was very light in intensity and intermittent in time. Exchange effects between the sample in the collection pan and the water vapour in the air could have given the nearly constant del values due to the long sampling times. The cause of the higher del values at the end is undetermined.

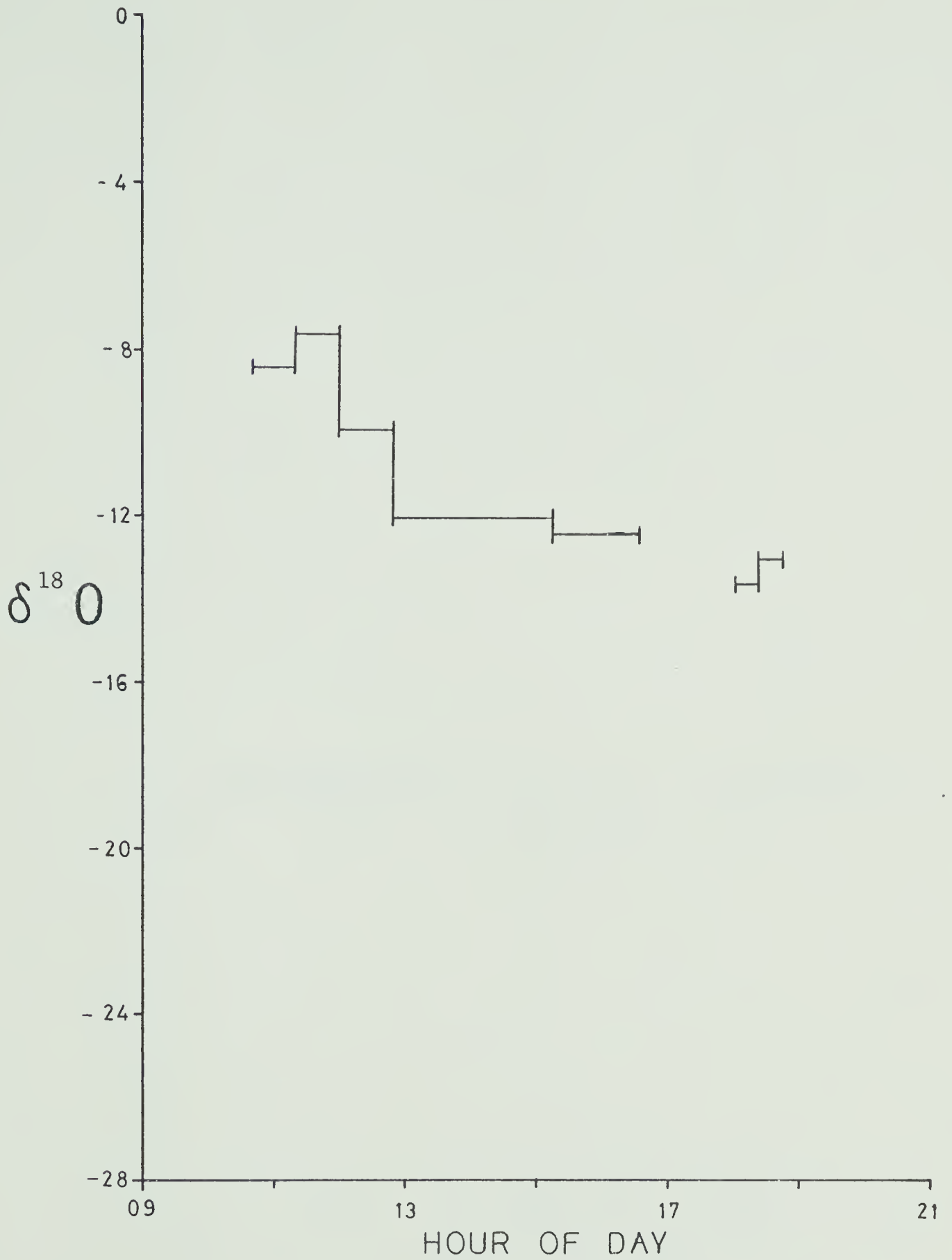


Figure 14. Time variations in $\delta^{18}O$ values of precipitation associated with warm frontal rain on September 1, 1970.

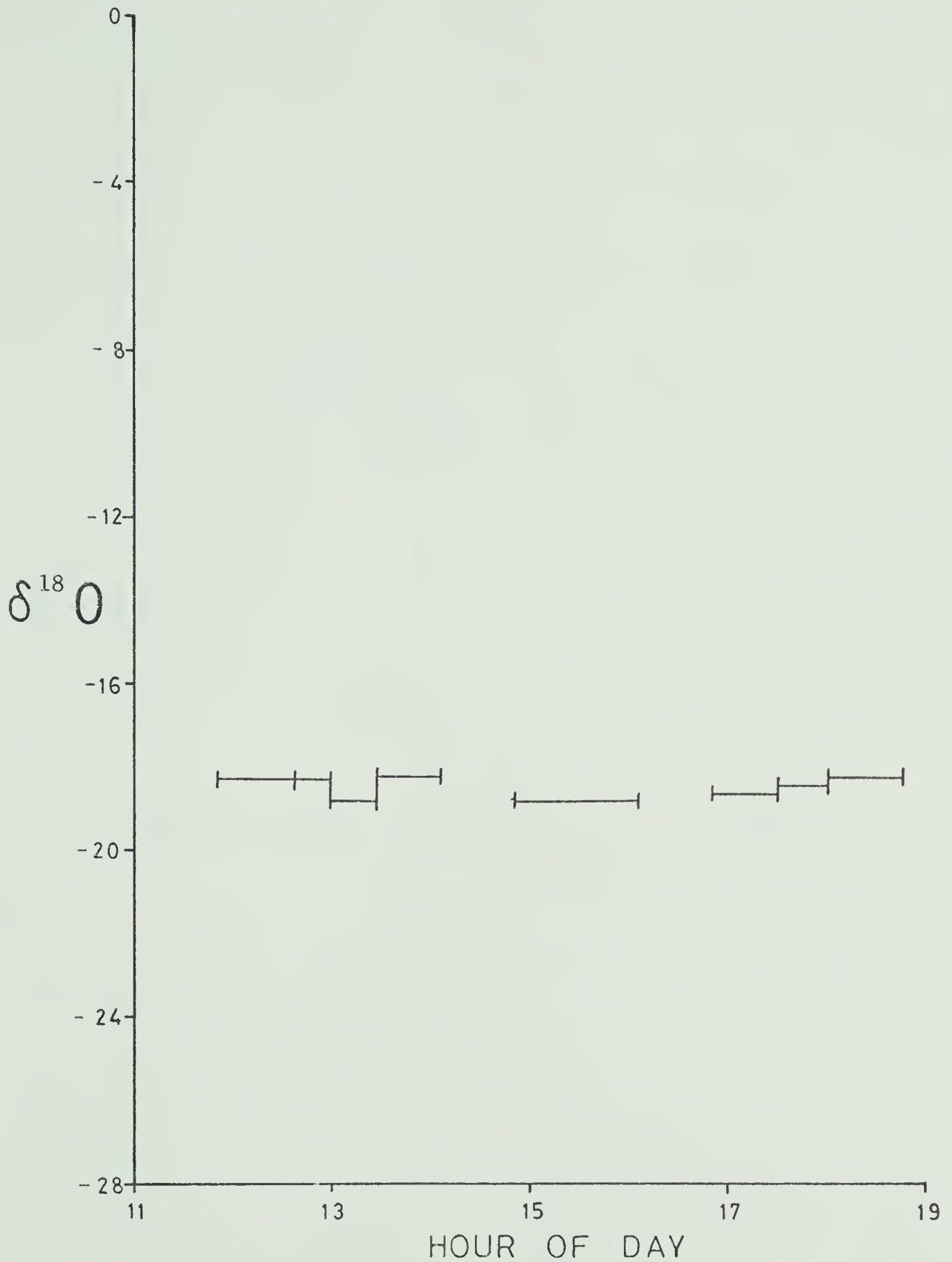


Figure 15. Time variations in $\delta^{18}O$ values of precipitation associated with cold low precipitation on June 5, 1971.

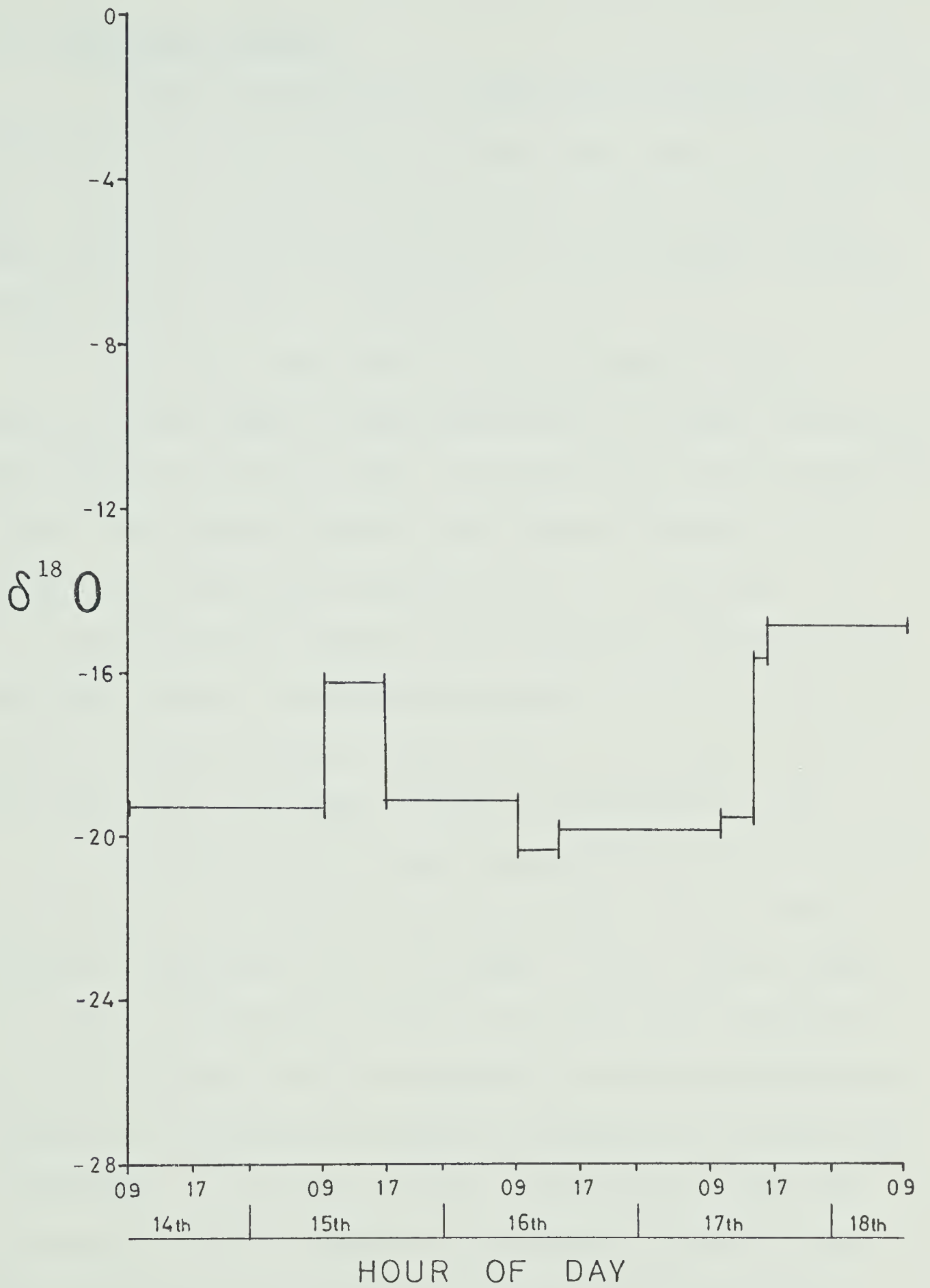


Figure 16. Time variations in $\delta^{18}O$ values of precipitation associated with cold-low precipitation on June 14-18, 1971.

5.4 An alternate Approach

It has been shown that in shower-type precipitation the oxygen ratio decreases with time. As mentioned, part of this decrease with time can be attributed to the reservoir effect in the cloud. Additionally, the cloud conditions can be used to provide a further insight into the observed variations.

Byers and Braham (1948) proposed a model for the life cycle of a heavy shower or thunderstorm cloud. The model consisted of three stages; the cumulus stage, the mature stage, and the dissipating stage. In the cumulus stage the cloud exhibited updrafts in all regions with cloud droplet growth but with no precipitation. In the mature stage there existed a zone of downdrafts associated with heavy precipitation, with updrafts maintained in other areas in the cloud. The final dissipative stage of the cloud contained downdrafts throughout with lighter intensity precipitation falling.

In order to model oxygen isotope variations in precipitation from a cloud of this type an atmosphere having a constant wetbulb potential temperature of 20 C was assumed. It was further assumed that in the mature stage the zone of downdrafts that contained the heavy precipitation could be represented by saturated-pseudoadiabatic cooling with a liquid water content of two grams per cubic meter and a cloud base at approximately fourteen hundred meters (cloud base temperature of 12 C). Similarly the dissipative stage was represented by saturated-pseudoadiabatic cooling with a liquid water content of one-half gram per cubic meter and a cloud base at approximately five hundred meters (cloud base temperature of 16 C). The

del value of the cloud droplets at 0 C in the cloud was presumed to be representative of the del values of the raindrops when they reached the base of the cloud for both stages.

In all calculations an initial vapour del value of -19.1 ppt was considered. This corresponded to the vapour del value if water with a del value of -10.0 ppt was evaporated under equilibrium conditions at 20 C, or alternatively to water with a del value of -19.1 ppt that underwent evapotranspiration. Eriksson (1965) stated that during evapotranspiration no fractionation can occur in this process because the very minute size of the capillary network of the evaporating medium permits no mixing to occur.

The effect of changing the liquid water content of the cloud proposed for the mature stage is shown in Figure 17. The lines drawn are for liquid water contents of 2.0, 1.0, and 0.5 grams per cubic meter. A change of 0.8 ppt at 0 C was noted. The variation caused by changing the cloud base temperature for a constant liquid water content is shown in Figure 18. At 0 C a change of 2.6 ppt occurred for the conditions shown in this example. Figure 19 shows the results of combining these effects of liquid water content and cloud base temperature. This yielded a total change of -2.3 ppt between the conditions chosen for the mature stage and for the dissipating stage.

Further modification of the ^{18}O content of the precipitation due to equilibrium exchange and evaporation between the cloud base and the ground must also be considered. Figure 20 shows the final del values for drops of different radii for the atmospheric conditions

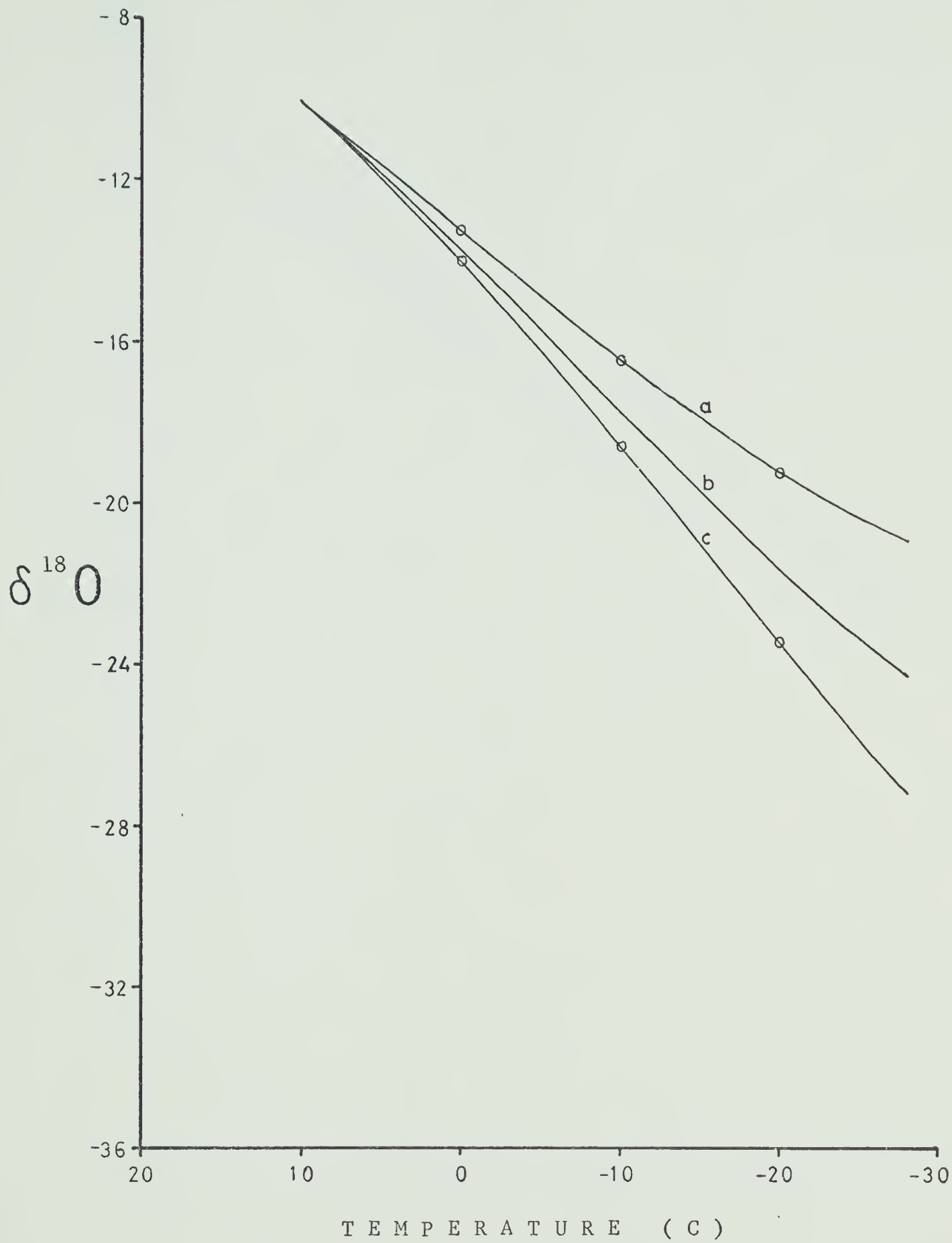


Figure 17. The effect of liquid water content on the $\delta^{18}O$ values of cloud droplets during cooling. Model 3. LWC of 2.0 (a), 1.0 (b), and 0.5(c). Cloud base temperature of 12 C.

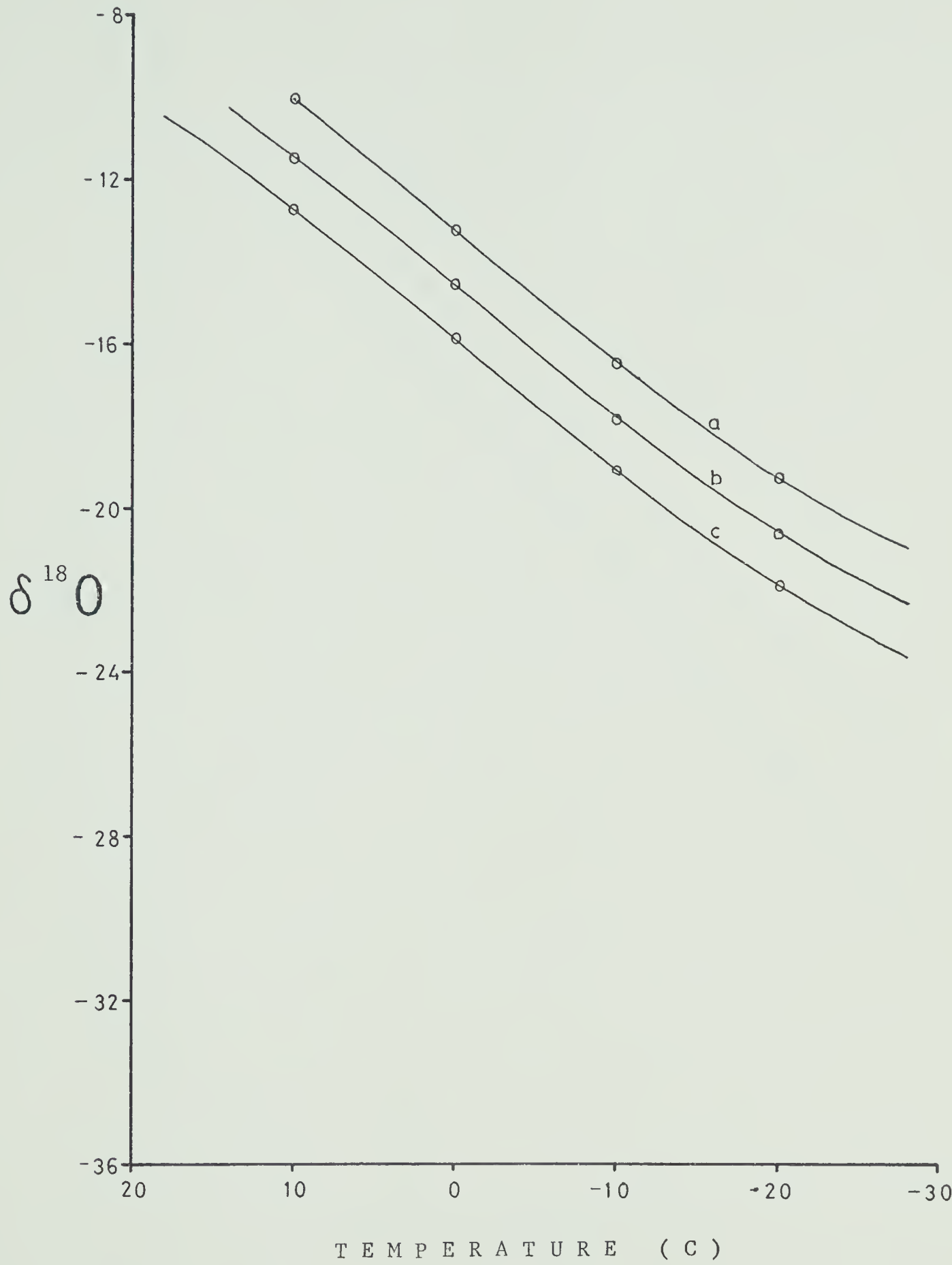


Figure 18. The effect of cloud base temperature on the δ^{18} values of cloud droplets during cooling. Model 3. Cloud base temperatures of 12 C (a), 16 C (b), and 20 C (c). LWC of 2.0 .

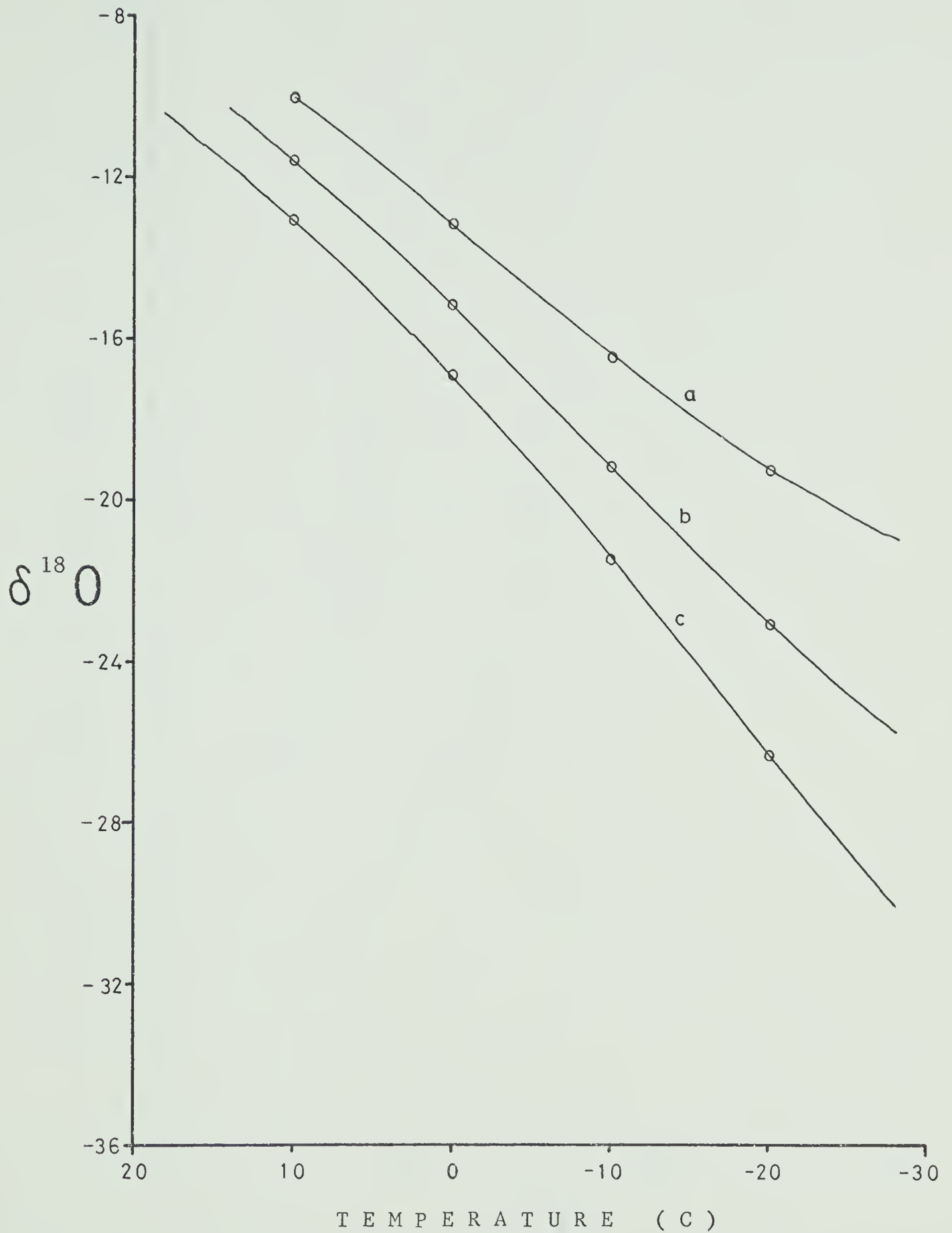


Figure 19. The combined effect of liquid water content and cloud base temperature on the $\delta^{18}O$ values of cloud droplets during cooling. T of 12 C, LWC of 2.0 (a); T of 16 C, LWC of 1.0 (b); and T of 20 C, LWC of 0.5 (c).

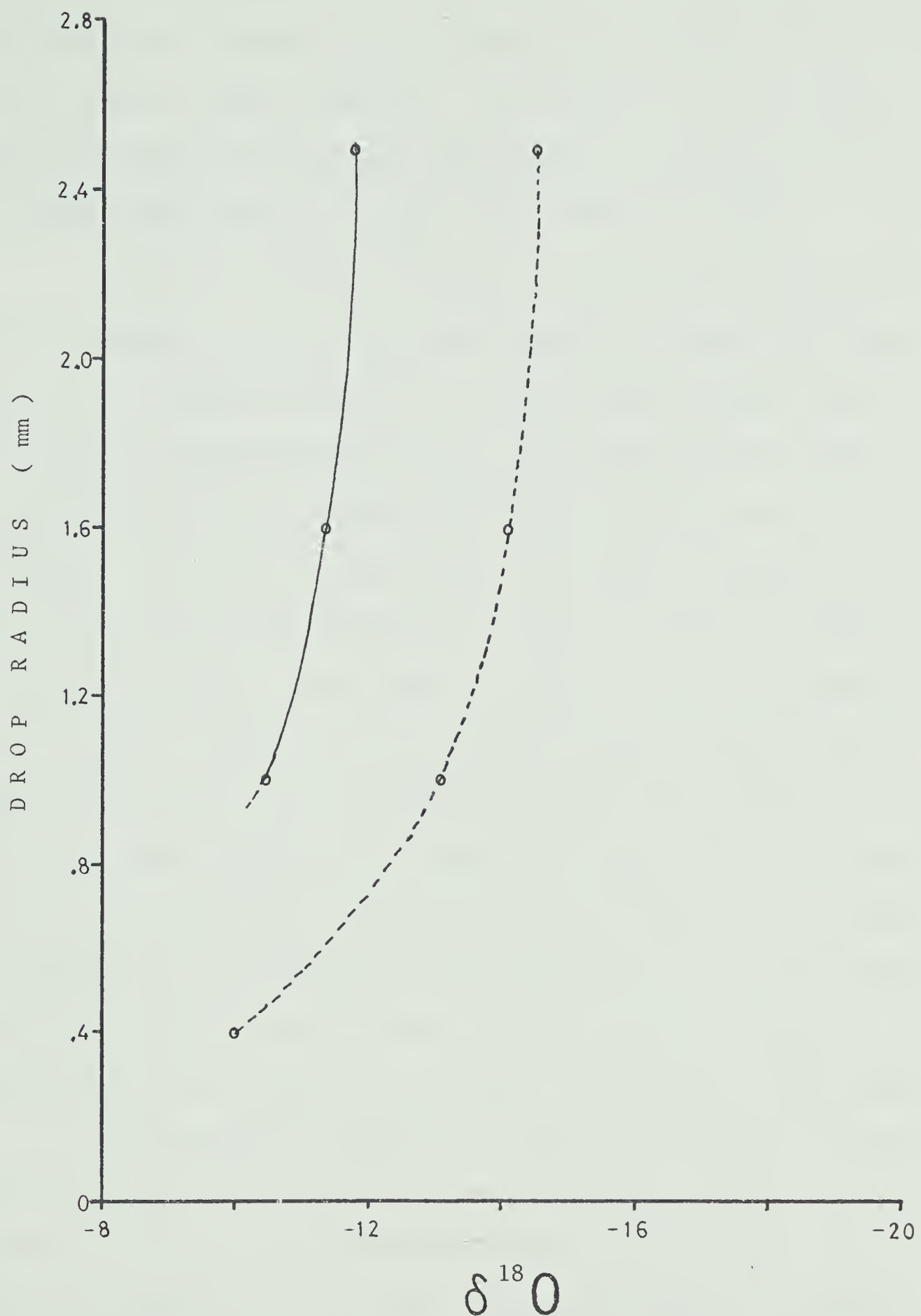


Figure 20. Final $\delta^{18}O$ values of raindrops due to equilibrium exchange. Solid line for mature stage, dashed line for dissipating stage.

described above, examining only the equilibrium exchange with the vapour in the air below cloud base. This resulted in a final Δe value difference of near 2.7 ppt between drops of the same radius in the mature stage compared to drops in the dissipative stage.

Figure 21 displays the results of equilibrium evaporation for the raindrops. Because the mature stage has a higher cloud base and a drier atmosphere below, the drops experience a larger evaporation than for the dissipating stage. This effect is more marked for the smaller drops as a larger percentage of these drops is evaporated. The final Δe values show differences of between 2.8 and 3.8 ppt for the radii considered. Kinetic evaporation is shown in Figure 22. This process yielded even larger differences, ranging up to 4.5 ppt. A summary of the results is shown in Table 2. This table includes the effect of changing the initial Δe values of the drops. The values shown are the change in the final Δe value expressed as a percentage of the change in the initial value. These values are dependent on the atmospheric conditions below the cloud base, and are shown for both the mature stage and the dissipating stage.

Figure 23 shows this change in percentage with radius for both stages.

The modelling as described in Chapter III did not allow for combining these results of exchange and evaporation. A conservative estimate of combining them gives a difference of 3 to 4 ppt, as the effects of evaporation will slightly reduce the effects of exchange, but not vice-versa. Thus this proposal is seen to produce results of the right order of magnitude.

TABLE 2

Summary of the changes of del values that occurred below cloud base, including the effect of a change of initial drop concentrations. Values shown are the final del values of the drops, and the change that occurred between the two stages.

PROCESS	FINAL DROP DEL VALUE BELOW CLOUD BASE				EFFECT OF CHANGING INITIAL CONCENTRATION	
	RADIUS	MATURE STAGE	DISSIPATING STAGE	CHANGE	MATURE STAGE	DISSIPATING STAGE
	mm			ppt	%	%
EQUILIBRIUM EXCHANGE	1.0	-10.5	-13.1	-2.6	21.7	57.8
	1.6	-11.3	-14.1	-2.7	45.6	74.8
	2.5	-11.8	-14.5	-2.7	59.5	82.4
EQUILIBRIUM EVAPORATION	1.0	-11.5	-15.3	-3.8	100	100
	1.6	-12.3	-15.4	-3.1	100	100
	2.5	-12.6	-15.4	-2.8	100	100
KINETIC EVAPORATION	1.0	-9.5	-14.0	-4.5	61.8	79.4
	1.6	-10.9	-14.6	-3.7	76.1	87.9
	2.5	-11.5	-14.9	-3.4	82.8	91.7

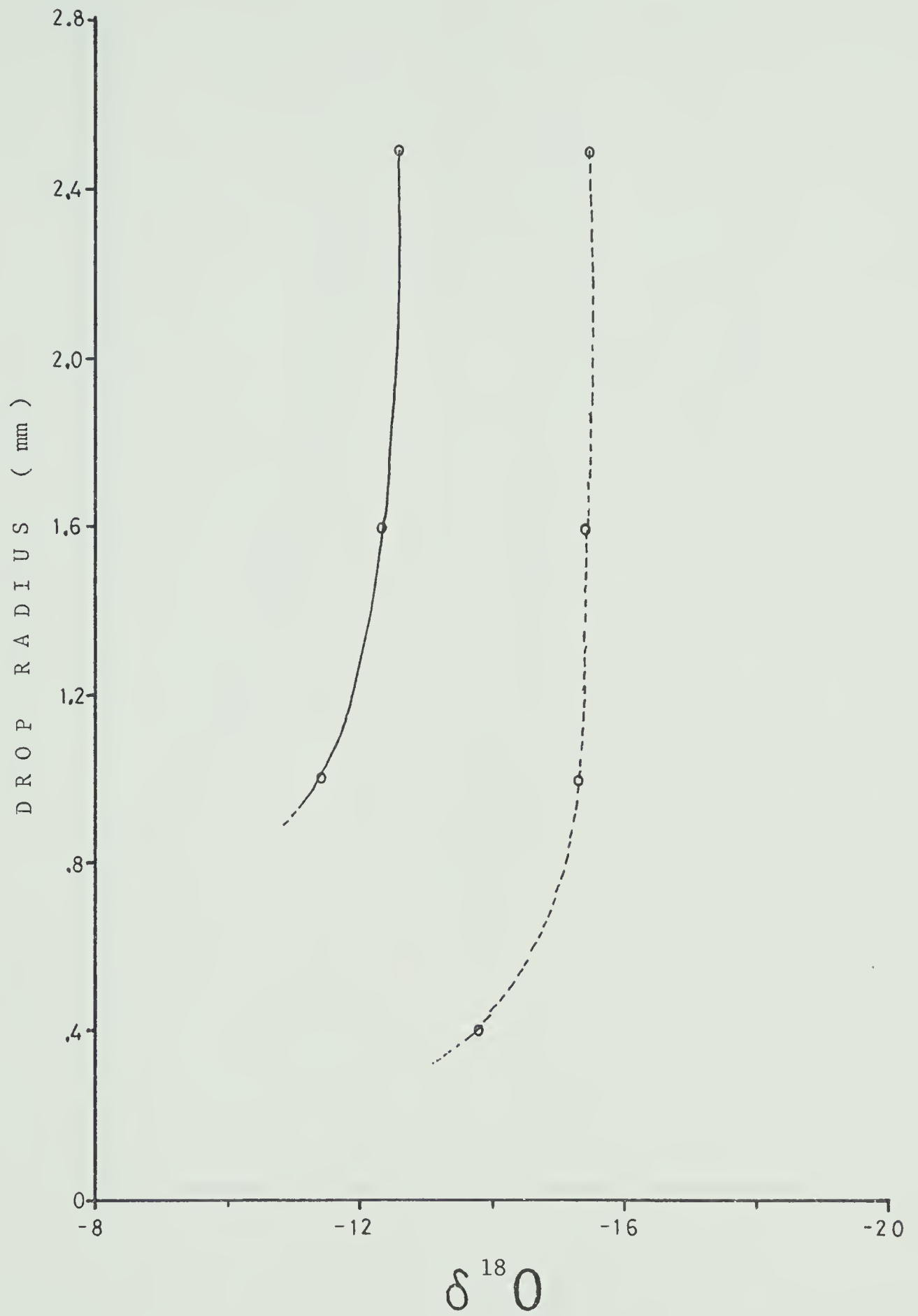


Figure 21. Final del values of raindrops due to equilibrium evaporation. Lines as for Figure 20.

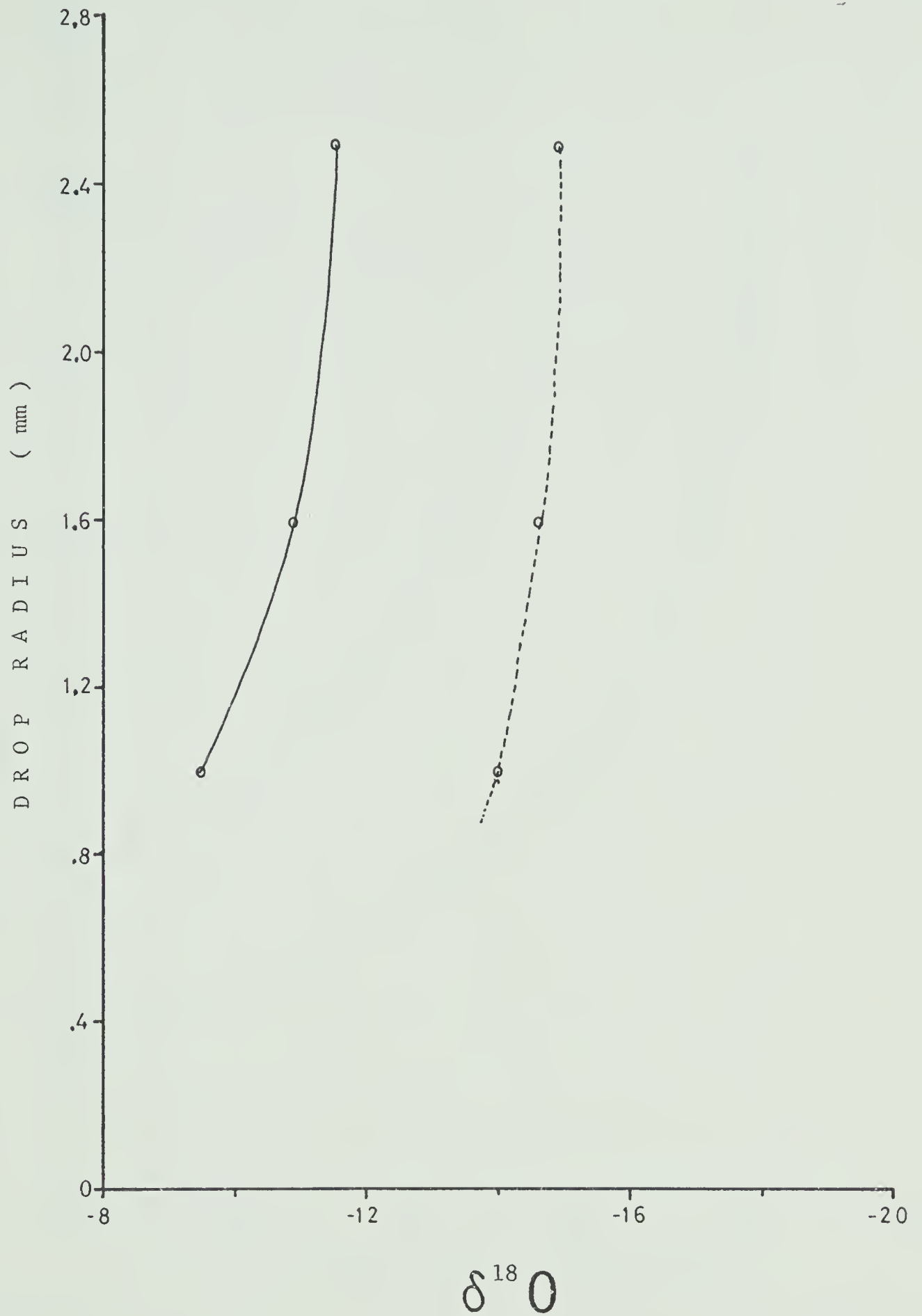


Figure 22. Final $\delta^{18}O$ values of raindrops due to kinetic evaporation. Lines as for Figure 20.

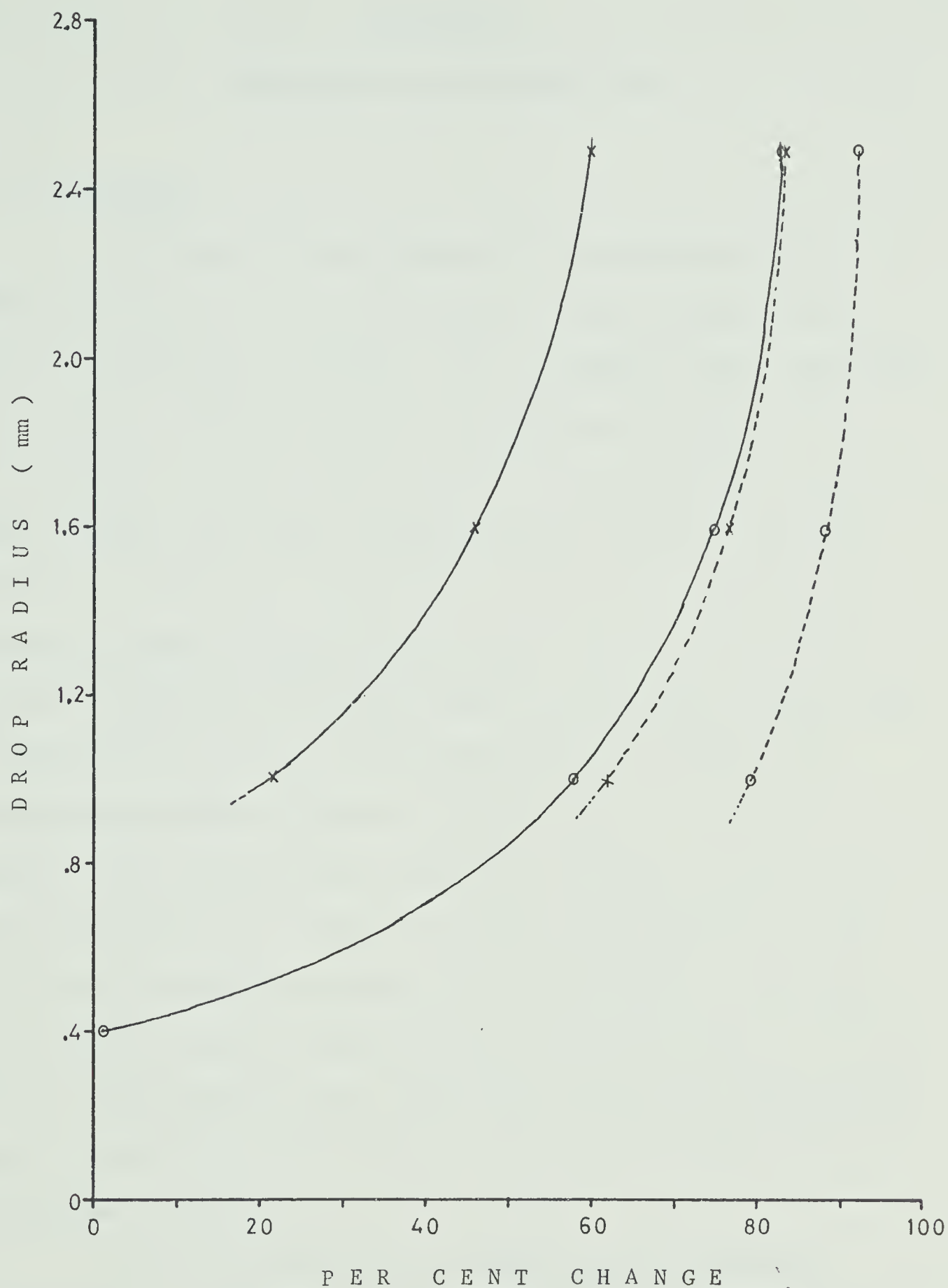


Figure 23. Percentage of the initial change in $\Delta \ell$ value of raindrops exhibited by the final raindrops. Solid lines are for exchange, dashed lines for kinetic evaporation. (X) mature stage, (O) dissipating stage.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In Chapter I it was shown that mean monthly data for Edmonton, Alberta did not fit Dansgaard's (1964) regression (Eq. (1.1)), but rather followed Eq. (1.2). It must be again noted that Eq. (1.1) was obtained using mean annual values while Eq. (1.2) was obtained using mean monthly values for only the summer months. Again assuming that similar regressions would result using either method, two conclusions can be drawn. Firstly, the difference in constants between the two relations implies that precipitation in Alberta is depleted in ^{18}O with respect to the coastal stations used in determining Eq. (1.1). This depletion may be regarded as a continentality effect (caused by a type of reservoir effect). Secondly, the decreased slope of Eq. (1.2) compared with Eq. (1.1) can be attributed to a change in the type of precipitation. Thus while coastal stations experience mainly precipitation associated with organised weather systems, continental stations such as Edmonton receive more instability type precipitation during the summer months and thus experience a wider range of types of precipitation than do the coastal stations.

It has been shown that by making certain simplifying assumptions it is possible to explain part of the variations that occurred in the data collected. However, because of the assumptions made, it was possible to show only the qualitative effects and general trends for the causes of variations listed in Chapter I.

Thus it is not possible to remove the variations due to local effects from the data to enable the ^{18}O to be used as a tracer for the water vapour.

Studies of changes in δ values with time within individual precipitation periods have shown several features. In most cases studied the effect of evaporation enriching the precipitation in ^{18}O for at least part of the time has been demonstrated. Also demonstrated to a lesser degree was the effect of exchange. By the use of a cloud model the marked decrease in time of ^{18}O concentration associated with airmass thunderstorms was demonstrated.

6.2 Recommendations for Further Studies

The nearly constant δ values with time measured in general precipitation do not exclude the possibility of exchange during collection affecting the samples. Thus the collection methods must be reviewed and improved to minimize the effects of evaporation during collection and of exchange with the water vapour in the air. In this way a check of the observed constancy in the precipitation δ values can be made to see if this is a natural phenomenon.

The practical use of the models developed requires some method of sampling the water vapour in the air. Thus some method of collecting these samples must be developed. The collection of cloud droplet samples would help to complete the observational network, although this could prove to be a monumental task. It is also recommended that Hydrogen isotopic analysis of the samples be undertaken, because the relation between Deuterium and ^{18}O concentrations

gives a measure of the relative importance of the kinetic processes that occur (Dansgaard, 1964).

The models that have been developed may prove useful in other fields of study. As mentioned in Chapter I, some work has been done in the last few years using ^{18}O in the study of hailstones with models similar to the closed models developed. It is felt that the use of the open models developed would be more accurate for this work. By expanding and further developing the ideas expressed for convective storms it may prove possible to use ^{18}O as an independent check for numerical models for clouds that are being developed for other uses.

While at the present time it is impossible to use ^{18}O as a tracer for the water vapour, it is hoped that the models developed can be used in future studies with a more complete set of data to investigate this possibility.

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A P P E N D I X A

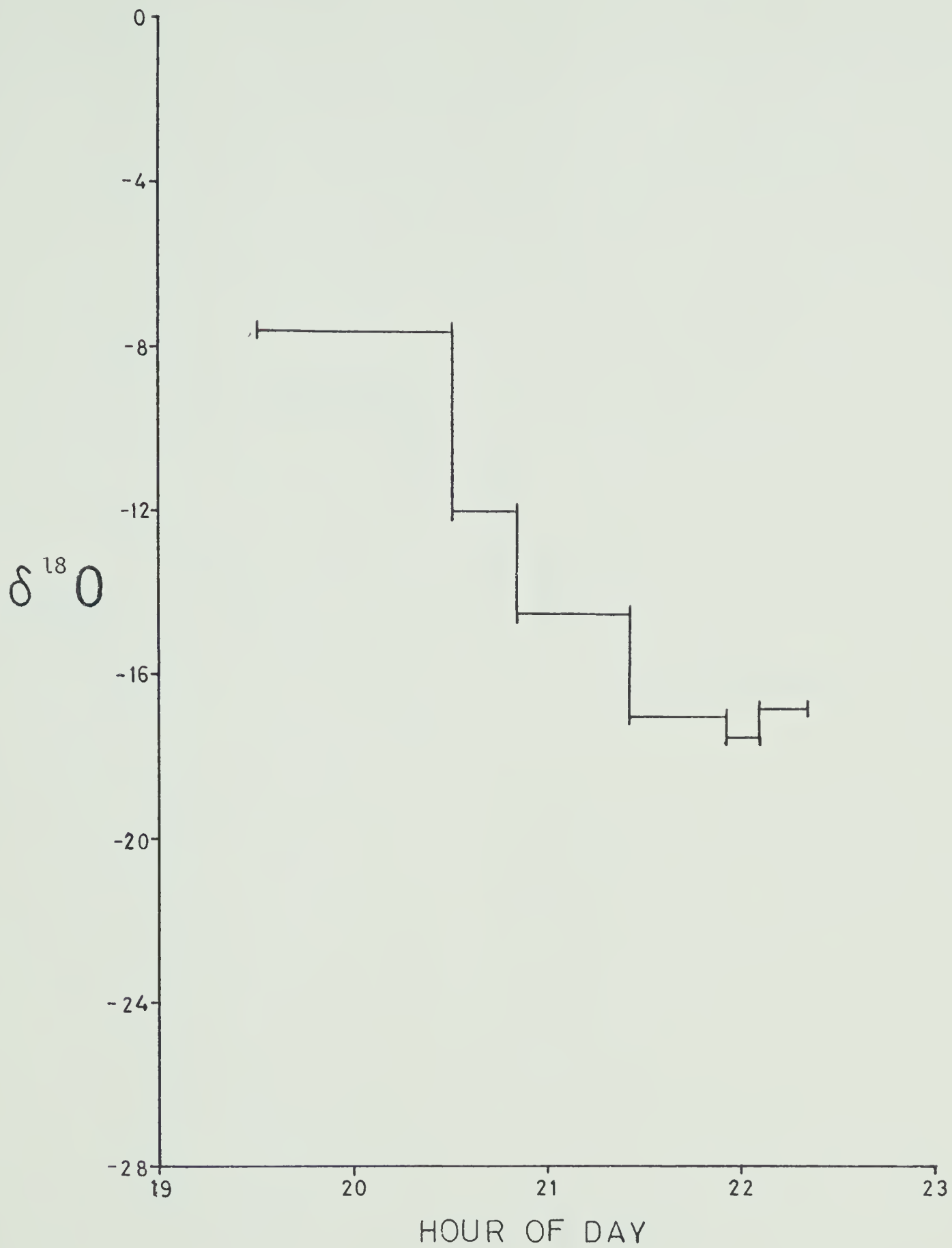


Figure A-1. Time variations in $\delta^{18}O$ values of precipitation associated with an airmass thunderstorm on July 20, 1970.

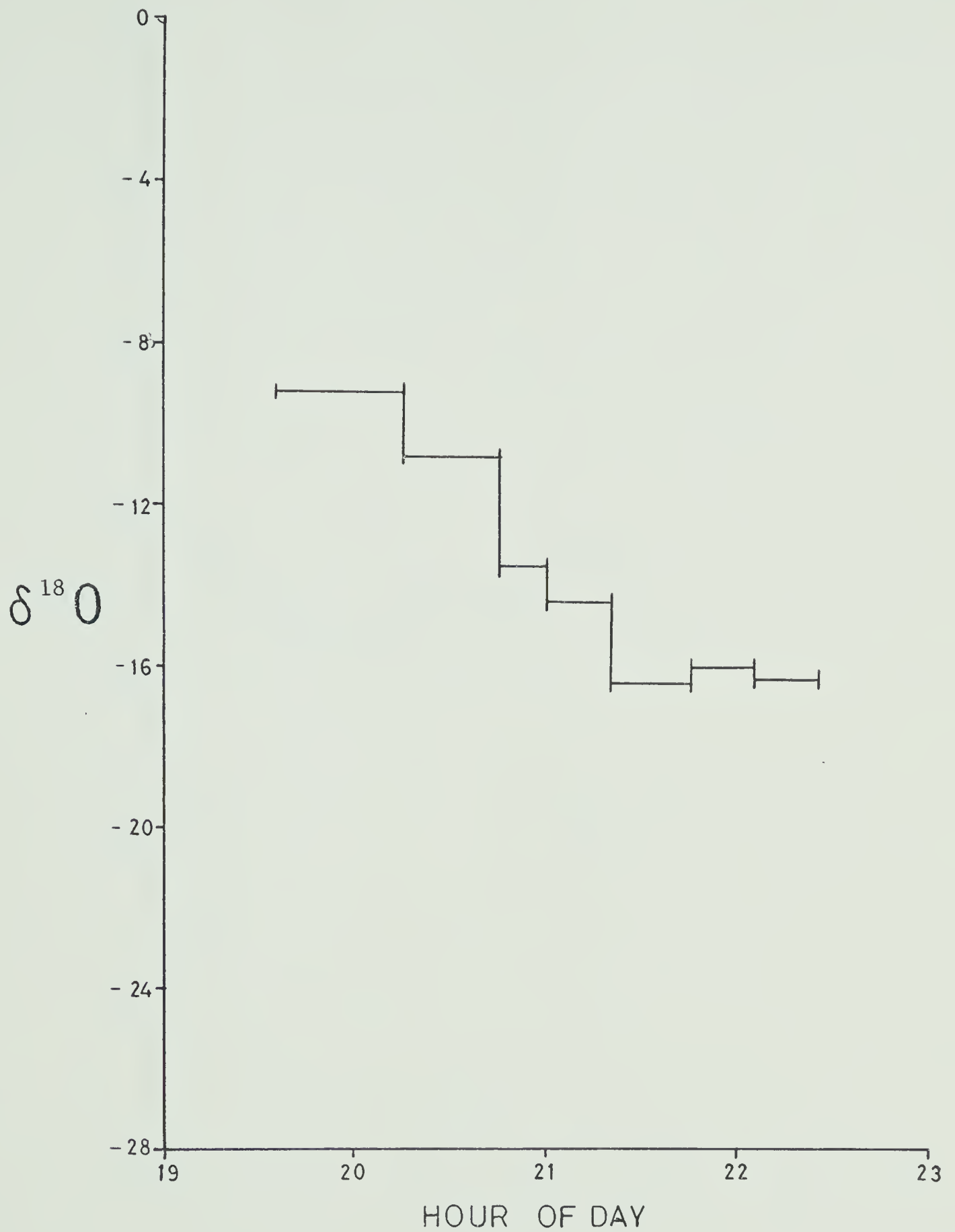


Figure A-2. Time variations in $\delta^{18}O$ values of precipitation associated with an airmass thunderstorm on July 20, 1970. (Different observing site than for Figure A-1.)

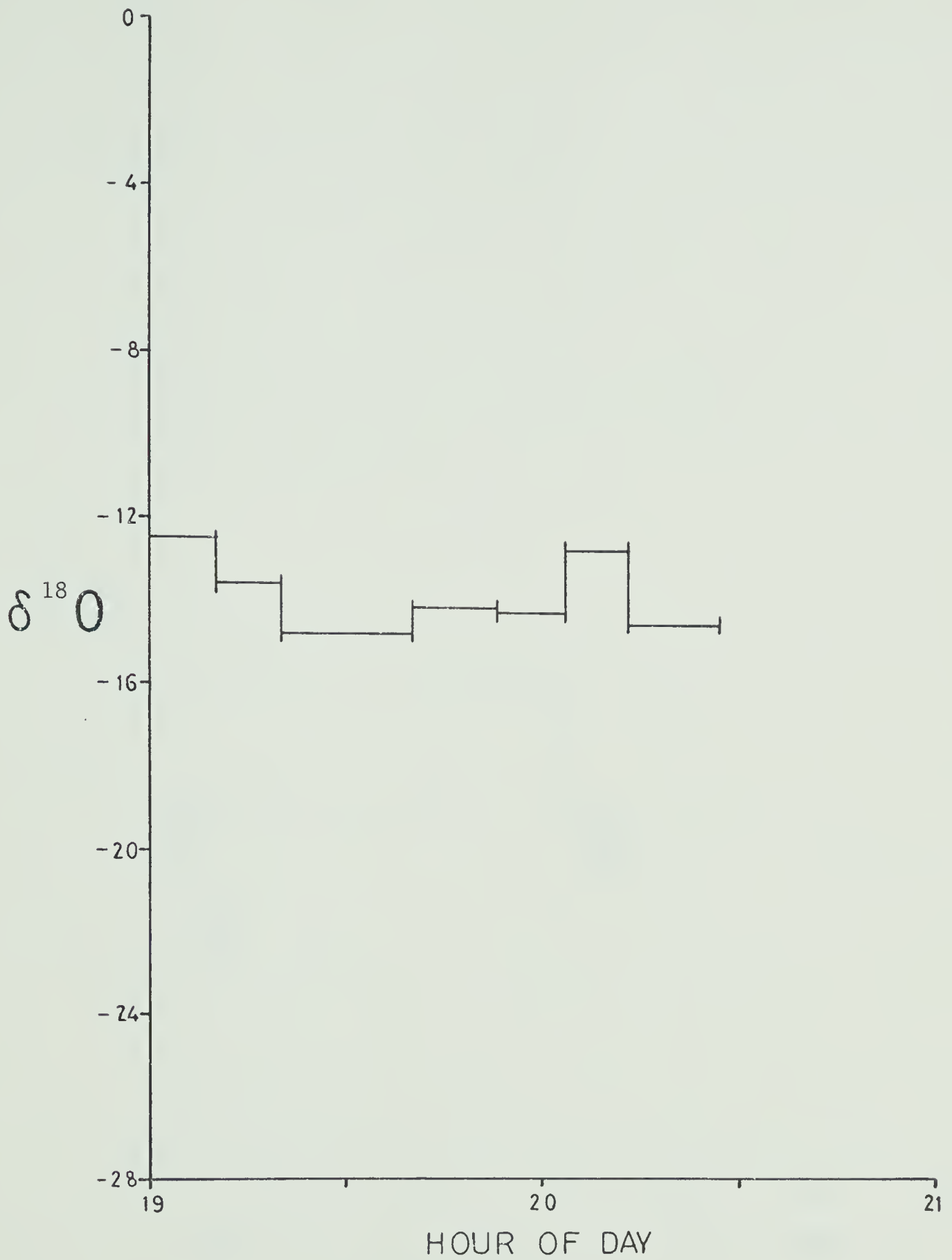


Figure A-3. Time variations in $\delta^{18}O$ values of precipitation associated with a non-airmass thunderstorm on July 9, 1970.

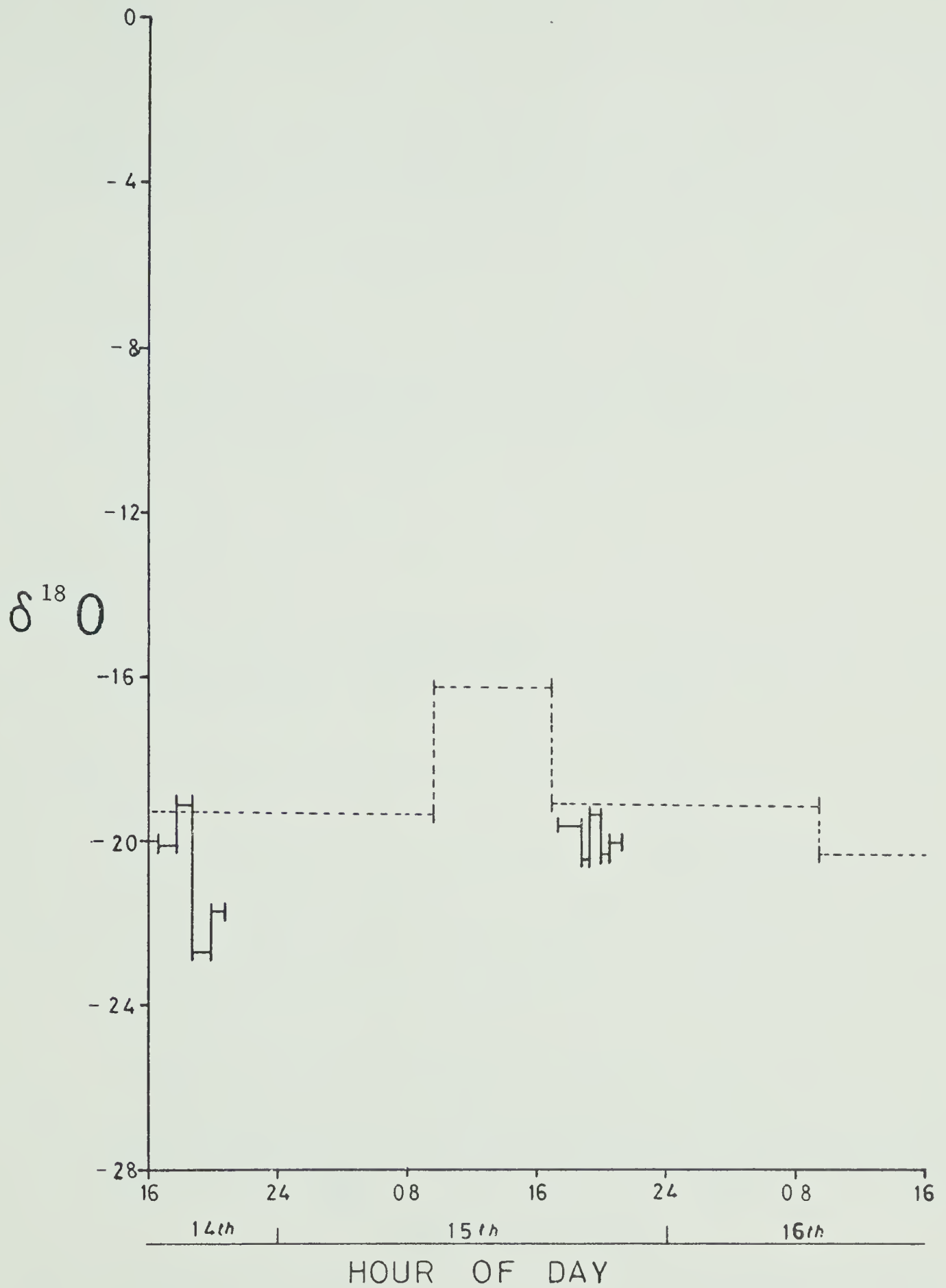


Figure A-4. Time variations in $\delta^{18}\text{O}$ values of precipitation associated with a period of general rain on June 14-16, 1971. Dashed and solid lines indicate different observing sites.

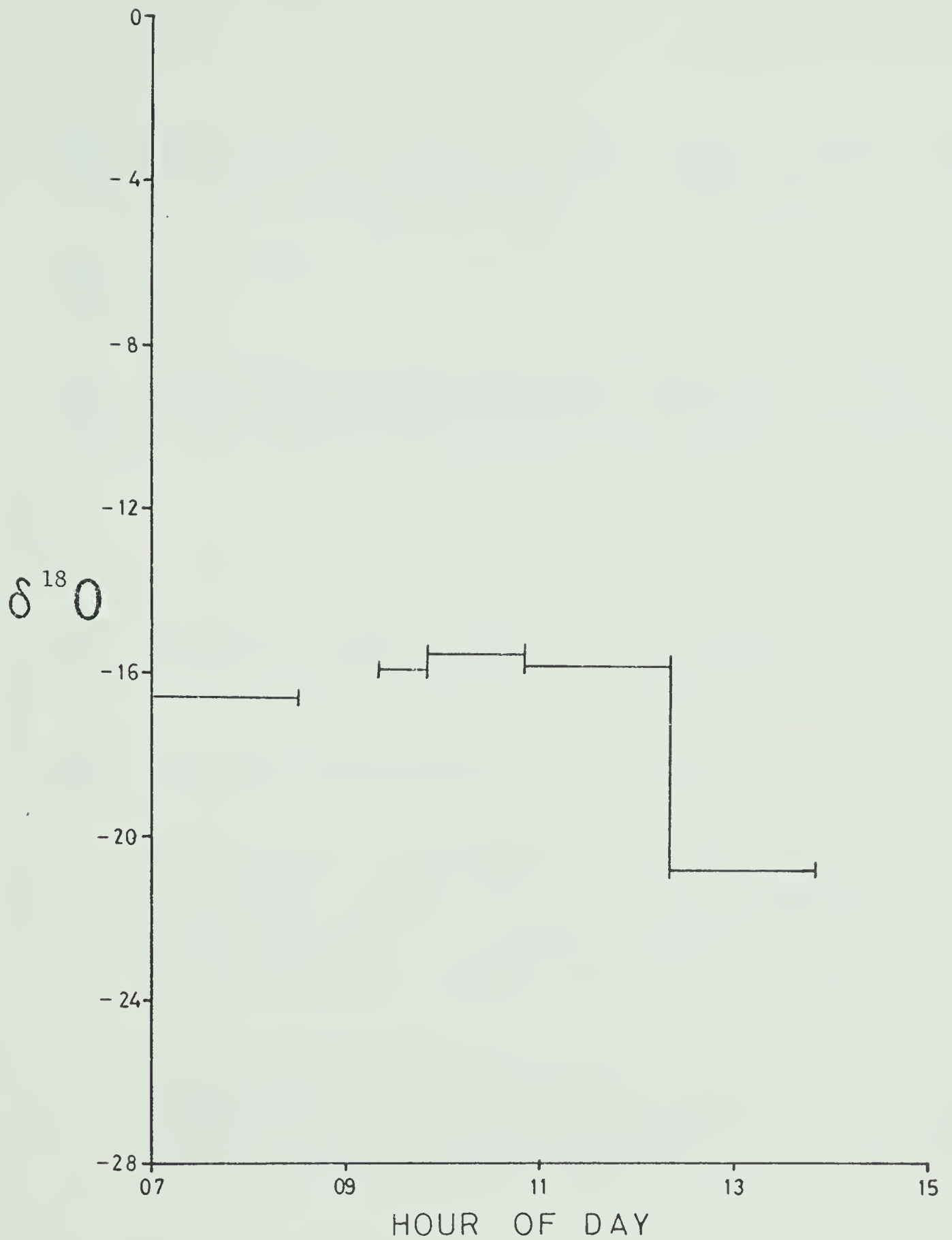


Figure A-5. Time variations in $\delta^{18}O$ values of precipitation associated with a period of general rain on July 29, 1970.

TABLE A-1
A listing of all samples collected

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DEL SAMPLE	DEL STND	SITE CODE
5001	30/06/70	11:24-13:01	61	8.8	.	-16.9	.	03
5002	30/06/70	13:01-14:26	61	9.0	.	-16.9	.	03
5003	30/06/70	14:26-15:41	61	9.0	.	-20.6	.	03
5004	09/07/70	19:00-19:10	95	24.0	.	-12.5	.	01
5005	09/07/70	19:10-19:20	95	23.5	.	-13.6	.	01
5006	09/07/70	19:20-19:40	95	20.0	.	-14.8	.	01
5007	09/07/70	19:40-19:53	95	16.0	.	-14.2	.	01
5008	09/07/70	19:53-20:04	95	16.0	.	-14.3	.	01
5009	09/07/70	20:04-20:13	95	16.0	.	-12.8	.	01
5010	09/07/70	20:13-20:28	95	15.7	.	-14.6	.	01
5011	09/07/70	: -19:40	95	15.8	.	-15.5	.	02
5012	09/07/70	19:40-22:30	80	16.0	.	-14.3	.	02
5013	10/07/70	19:00-23:00	61	19.0	.	-11.5	.	02
5015	11/07/70	16:00-18:00	61	17.0	.	-12.8	.	02
5016	11/07/70	17:02-17:08	95	.	.	-14.5	.	07
5017	11/07/70	17:08-17:15	95	.	.	-14.8	.	07
5018	11/07/70	17:15-17:18	95	.	.	-16.2	.	07
5019	11/07/70	17:18-17:25	95	.	.	-12.4	.	07
5020	20/07/70	19:35-20:15	61	17.0	.	-9.2	.	01
5021	20/07/70	20:15-20:45	61	17.0	.	-10.8	.	01
5022	20/07/70	20:45-21:00	63	16.0	.	-13.5	.	01
5023	20/07/70	21:00-21:20	63	16.0	.	-14.4	.	01
5024	20/07/70	21:20-21:45	95	15.0	.	-16.4	.	01
5025	20/07/70	21:45-22:05	95	15.0	.	-16.0	.	01
5026	20/07/70	22:05-22:25	95	14.7	.	-16.3	.	01
5032	20/07/70	19:30-20:30	61	17.7	.	-7.6	.	02
5033	20/07/70	20:30-20:50	63	17.0	.	-12.0	.	02
5034	20/07/70	20:50-21:25	61	16.0	.	-14.5	.	02
5035	20/07/70	21:25-21:55	95	15.0	.	-17.0	.	02
5036	20/07/70	21:55-22:05	95	15.0	.	-17.5	.	02
5037	20/07/70	22:05-22:20	95	14.9	.	-16.8	.	02

TABLE A-1 cont.

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DEL SAMPLE	DEL STND	SITE CODE
5027	29/07/70	07:00-08:30	61	10.5	.	-16.6	.	01
5028	29/07/70	09:20-09:50	61	11.5	.	-15.9	.	03
5029	29/07/70	09:50-10:50	61	12.0	.	-15.5	.	03
5030	29/07/70	10:50-12:20	61	12.7	.	-15.8	.	03
5031	29/07/70	12:20-13:50	61	11.8	.	-20.8	.	03
5046	08/08/70	09:50-10:00	95	.	.	-10.0	.	08
5047	08/08/70	10:02-10:03	95	.	.	-09.6	.	08
5048	08/08/70	10:08-10:09	95	.	.	- 9.9	.	08
5049	08/08/70	10:18-10:19	95	.	.	-10.8	.	08
5050	08/08/70	10:10- :	00	18.0	.	- 9.6	.	09
5051	08/08/70	10:10- :	00	18.0	.	- 9.8	.	09
5052	08/08/70	10:10- :	00	18.0	.	-10.1	.	09
5053	08/08/70	10:10- :	00	18.0	.	- 9.3	.	09
5038	13/08/70	: -07:30	95	13.5	.	-16.4	.	02
5039	13/08/70	07:30-07:31	95	13.0	.	-17.3	.	02
5040	13/08/70	07:31-07:45	95	12.5	.	-17.8	.	02
5041	13/08/70	07:45-07:52	95	12.0	.	-19.1	.	02
5042	13/08/70	07:52-08:00	95	12.0	.	-18.3	.	02
5043	13/08/70	08:00-08:12	81	12.0	.	-18.2	.	02
5044	13/08/70	08:12-08:28	81	12.1	.	-18.7	.	02
5045	13/08/70	08:28-09:07	80	12.2	.	-16.9	.	02
5054	25/08/70	22:31-22:54	80	13.0	.	-11.4	.	01
5055	01/09/70	10:40-11:20	61	13.5	.	- 8.4	.	03
5056	01/09/70	11:20-12:00	61	13.5	.	- 7.6	.	03
5057	01/09/70	12:00-12:50	60	13.8	.	- 9.9	.	03
5058	01/09/70	12:50-15:15	60	14.0	.	-12.0	.	03
5059	01/09/70	15:15-16:35	60	13.8	.	-12.4	.	03
5060	01/09/70	18:03-18:21	61	11.8	.	-13.6	.	01
5061	01/09/70	18:21-18:45	61	11.7	.	-13.0	.	01

TABLE A-1 cont.

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DEL SAMPLE	DEL STND	SITE CODE
5088	24/11/70	18:15-	71	-15.5	.	-28.2	.	01
5089	24/11/70	18:15-	71	-15.5	.	-29.3	.	01
5090	24/11/70	18:15-	71	-15.5	.	-29.2	.	01
5091	24/11/70	18:15-	71	-15.5	.	-30.0	.	01
5092	24/11/70	19:15-	71	-15.7	.	-29.8	.	01
5093	24/11/70	19:15-	71	-15.7	.	-29.5	.	01
5094	24/11/70	19:15-	71	-15.7	.	-29.9	.	01
5095	24/11/70	21:30-	71	-16.0	.	-33.8	.	01
5096	24/11/70	21:30-	71	-16.0	.	-32.3	.	01
5097	24/11/70	21:30-	71	-16.0	.	-31.9	.	01
5098	03/12/70	19:15-	71	-24.0	.	-31.0	.	01
5099	03/12/70	19:15-	71	-24.0	.	-31.1	.	01
5100	03/12/70	21:00-	71	-24.0	.	-30.4	.	01
5101	03/12/70	21:00-	71	-24.0	.	-31.2	.	01
5102	03/12/70	22:20-	71	-24.0	.	-30.7	.	01
5103	03/12/70	22:20-	71	-24.0	.	-29.9	.	01

TABLE A-1 cont.

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DEL SAMPLE	DEL STND	SITE CODE
JL 001	22/05/71	16:04-16:10	81	17.0	1.000473	-14.7	-19.3	04
JL 002	22/05/71	16:10-16:23	80	13.0	1.000698	-12.5	-19.3	04
JL 003	27/05/71	16:30-16:40	81	15.0	1.000601	-13.4	-19.3	04
JL 004	27/05/71	16:40-16:48	81	13.0	1.000594	-13.5	-19.3	04
JL 005	27/05/71	16:48-16:53	81	11.5	1.000718	-12.3	-19.3	04
JL 006	27/05/71	16:53-17:56	80	10.0	1.000563	-13.8	-19.3	04
JL 007	04/06/71	11:05-12:55	61	15.9	1.00108	-18.2	-19.3	03
JL 008	05/06/71	11:50-12:37	61	14.0	1.00106	-18.3	-19.3	04
JL 009	05/06/71	12:37-12:58	61	14.0	1.00105	-18.3	-19.3	04
JL 010	05/06/71	12:58-13:27	61	14.1	1.00055	-18.8	-19.3	04
JL 011	05/06/71	13:27-14:05	61	14.3	1.00114	-18.2	-19.3	04
JL 012	05/06/71	14:50-16:05	61	14.2	1.00051	-18.8	-19.3	04
JL 013	05/06/71	16:50-17:30	61	13.9	1.00075	-18.6	-19.3	04
JL 014	05/06/71	17:30-18:00	61	13.9	1.00095	-18.4	-19.3	04
JL 015	05/06/71	18:00-18:45	61	14.1	1.00117	-18.2	-19.3	04
JL 016	05/06/71	19:00-21:30	61	14.1	1.00017	-19.1	-19.3	05
JL 017	08/06/71	11:55-14:15	61	13.0	1.00142	-17.9	-19.3	03
JL 019	11/06/71	20:00-07:30	80	12.8	0.99979	-19.5	-19.3	05
JL 020	12/06/71	20:00-07:30	80	14.5	1.00078	-18.5	-19.3	05
JL 018	14/06/71	02:00-02:30	95	10.0	1.00011	-19.2	-19.3	03
JL 021	14/06/71	16:40-17:45	61	10.6	0.99921	-20.1	-19.3	04
JL 022	14/06/71	17:45-18:45	61	10.2	1.00022	-19.1	-19.3	04
JL 023	14/06/71	18:45-19:55	61	9.9	0.99658	-22.7	-19.3	04
JL 024	14/06/71	19:55-20:50	61	9.6	0.99760	-21.7	-19.3	04
JL 025	14/06/71	16:00-20:00	61	8.9	1.00013	-19.2	-19.3	05
JL 026	14/06/71	20:00-24:30	61	8.1	0.99848	-20.8	-19.3	05
JL 027	14/06/71	09:00-33:30	61	10.2	1.00002	-19.3	-19.3	03

TABLE A-1 cont.

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DFL SAMPLE	DFL STND	SITE CODE
JL 028	15/06/71	09:30-16:50	60	11.4	1.00313	-16.2	-19.3	03
JL 029	15/06/71	17:15-18:45	61	12.1	0.99772	-19.6	-19.3	04
JL 030	15/06/71	18:45-19:15	61	10.8	0.99892	-20.4	-19.3	04
JL 031	15/06/71	19:15-19:55	61	10.6	1.00005	-19.3	-19.3	04
JL 032	15/06/71	19:55-20:25	61	10.1	0.99990	-20.3	-19.3	04
JL 033	15/06/71	20:25-21:05	61	9.9	0.99882	-20.0	-19.3	04
JL 034	15/06/71	14:00-19:15	61	11.1	1.00037	-19.0	-19.3	05
JL 035	15/06/71	19:45-21:00	61	9.1	0.99997	-19.4	-19.3	05
JL 036	15/06/71	21:00-08:00	60	7.9	1.00040	-18.9	-19.3	05
JL 037	15/06/71	16:45-09:15	60	9.5	1.00020	-19.1	-19.3	03
JL 038	16/06/71	09:15-14:15	60	12.0	0.99900	-20.3	-19.3	03
JL 041	16/06/71	14:15-10:25	60	11.8	0.99951	-19.8	-19.3	03
JL 052	16/06/71	08:00-20:00	80	10.8	1.00126	-18.1	-19.3	05
JL 045	16/06/71	20:00-20:30	80	11.5	1.00325	-16.1	-19.3	05
JL 042	17/06/71	10:25-14:25	80	14.1	0.99883	-19.5	-19.3	03
JL 043	17/06/71	14:25-15:55	80	13.2	1.00383	-15.6	-19.3	03
JL 044	17/06/71	15:55-09:10	80	11.0	1.00460	-14.8	-19.3	03
H 001	17/06/71	22:33-22:45	80	11.8	0.99360	-25.6	-19.3	01
H 002	19/06/71	17:18-17:25	95	.	1.00264	-16.7	-19.3	08
H 003	19/06/71	17:25-17:53	96	.	0.99887	-20.4	-19.3	08
H 004	19/06/71	17:53-18:28	95	.	1.00486	-14.5	-19.3	08
JL 046	23/06/71	07:00-09:30	61	14.1	1.00665	-12.8	-19.3	03
JL 047	23/06/71	09:30-16:40	60	12.5	1.00343	-16.0	-19.3	03
JL 048	23/06/71	16:40-09:45	60	10.5	1.00251	-16.8	-19.3	03
JL 049	23/06/71	17:05-17:40	80	15.6	1.00338	-16.0	-19.3	05
JL 050	23/06/71	17:40-19:15	61	15.0	1.00541	-14.0	-19.3	05
JL 051	01/07/71	16:50-17:15	89	21.5	0.99720	-22.1	-19.3	05
JL 053	02/07/71	10:10-12:00	61	9.5	1.00549	-13.9	-19.3	03
JL 054	10/07/71	16:30-24:00	80	13.0	1.00343	-15.9	-19.3	05
JL 055	09/07/71	11:07-71:	80	11.0	1.00622	-13.2	-19.3	03
JL 056	21/07/71	13:50-14:30	95	20.0	0.99680	-22.4	-19.3	05

TABLE A-1 cont.

NO.	DATE	TIME	WX CODE	TEMP (°C)	RATIO	DEL SAMPLE	DEL STND	SITE CODE
JL 057	23/07/71	16:35-17:05	95	18.0	1.00534	-14.1	-19.3	04
JL 058	23/07/71	17:05-17:35	95	16.5	1.00466	-14.7	-19.3	04
JL 059	23/07/71	17:35-17:55	95	15.0	1.00379	-15.6	-19.3	04
JL 060	23/07/71	17:55-18:20	95	13.0	1.00232	-17.0	-19.3	04
JL 061	23/07/71	18:20-18:45	95	12.7	1.00027	-19.1	-19.3	04
JL 062	23/07/71	18:45-20:40	80	12.5	0.99982	-19.5	-19.3	04
JL 063	23/07/71	16:30-22:00	95	14.2	1.00132	-18.0	-19.3	05
JL 064	26/07/71	18:00-19:00	80	20.0	1.00491	-14.5	-19.3	05
JL 065	03/08/71	21:25-21:35	89	20.0	1.00426	-15.1	-19.3	05
JL 066	03/08/71	21:30-21:40	99	15.9	1.00299	-16.4	-19.3	05
JL 067	03/08/71	21:40-22:30	95	15.8	1.00528	-14.1	-19.3	05
JL 068	18/09/71	12:00-17:00	80	16.3	0.99969	-19.6	-19.3	05
JL 069	19/09/71	09:30-11:15	60	7.0	1.00479	-14.6	-19.3	06
JL 070	19/09/71	11:15-12:00	61	6.2	0.99923	-20.1	-19.3	06
JL 071	19/09/71	12:00-14:30	61	6.0	0.99964	-19.7	-19.3	06

TABLE A-2

The site code

CODE	LOCATION
01	11504 - 37B AVENUE
02	11630 - 74 AVENUE
03	112 ST. & SASKATCHEWAN DRIVE
04	11130 - 57 AVENUE
05	17A MEADOWLARK VILLAGE
06	4029 - 112 AVENUE
07	SYLVAN LAKE
08	POPLAR BAY
09	PIGEON LAKE
10	SULPHUR MOUNTAIN
99	UNKNOWN

TABLE A-3

The weather (WX) code

CODE	WEATHER
00	WATER SAMPLE
60	LIGHT INTERMITTENT RAIN
61	LIGHT CONTINUOUS RAIN
62	MODERATE INTERMITTANT RAIN
63	MODERATE CONTINUOUS RAIN
70	LIGHT INTERMITTANT SNOW
71	LIGHT CONTINUOUS SNOW
80	LIGHT RAIN SHOWER
81	MODERATE OR HEAVY RAIN SHOWER
89	HAIL SHOWER
95	THUNDERSHOWER
96	THUNDERSHOWER WITH HAIL
97	HEAVY THUNDERSHOWER
99	HEAVY THUNDERSHOWER WITH HAIL

A P P E N D I X B

The equilibration of the carbon dioxide and water during sample preparation causes a change in the oxygen ratio of both the carbon dioxide and the water due to the finite masses used. To correct for this modification Craig (1957, p 144) gave

$$\delta_r = \delta_m \frac{(\rho + \alpha)}{\rho} - \frac{\alpha}{\rho} \delta_s \quad (\text{B.1})$$

where δ_r is the corrected δ value relative to the standard with a δ value of δ_s , δ_m is the measured δ value during analysis, and α is the fractionation factor for the equilibration process, given by

$$\alpha = C_{\text{carbon dioxide}} / C_{\text{water}} \quad (\text{B.2})$$

where C is the oxygen ratio in the carbon dioxide and in the water, and has a value of 1.039 at 25 C. ρ is the ratio of gram atoms of oxygen in the water sample to gram atoms of oxygen in the carbon dioxide introduced into the sample flask.

During preparation of the samples 1 to 2 ml of water were placed in a 25 ml flask that was then filled with carbon dioxide to a pressure of approximately 38 cm of mercury. Thus ρ has values of between 55.56 and 115.2; the values for 1 and 2 ml of water, respectively. With δ_s having a value of -19.3 ppt, Eq. (B.1) becomes

$$\delta_r = 1.019 \delta_m + 0.361 \text{ ppt}$$

for 1 ml of water, and

$$\delta_r = 1.009 \delta_m + 0.174 \text{ ppt}$$

for 2 ml of water. Considering an average of 1.5 ml of water (ρ equals 84.88), Eq. (B.1) becomes

$$\delta_r = 1.012 \delta_m + 0.236 \text{ ppt} \quad (\text{B.3})$$

This correction means that all δ values given must be increased by 0.24 ppt and that the actual δ values have a larger spread than the measured δ values.

Using one of the larger measured δ values (see Table A-1, sample no. JL 005) δ_m equals 7.18, and assuming a small volume of water used (1 ml), δ_r equals 7.68, giving a maximum error of 7 per cent in the relative δ value, or an error of 4 per cent in the δ value with respect to SMOW (-11.8 versus -12.3). Using Eq. (B.3) this becomes a likely error of 4 per cent (δ_r equals 7.43) in the relative δ value, or a likely error of 2 per cent in the δ value with respect to SMOW (-12.0 versus -12.3).

Because most samples had a smaller measured δ value, the error introduced by neglecting this correction factor was smaller.

B30029